Cement-Superplasticizer Interactions at Ambient Temperatures
Rheology, Phase Composition, Pore Water and Heat of Hydration of Cementitious Systems

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
for the degree of
Doctor of Technical Sciences

presented by
ANDREAS GRIESSER
Dipl. Natw. ETH Zürich
born on May 28, 1973
citizen of Weiach (ZH)

accepted on the recommendations of
Prof. Dr. H. Böhni, examiner
Prof. Dr. H. Hofmann, co-examiner
Dr. F. Hunkeler, co-examiner

Zurich 2002
# Table of Contents

Table of Contents ........................................................................................................... i
Abbreviations / Glossary ............................................................................................... v
Zusammenfassung ........................................................................................................ vii
Abstract ....................................................................................................................... xi

1 Introduction ................................................................................................................. 1
   1.1 General Overview ............................................................................................... 1
   1.2 Thesis Objectives .............................................................................................. 2

2 Literature .................................................................................................................... 5
   2.1 Introduction ....................................................................................................... 5
   2.2 Forces Affecting Small Particles ....................................................................... 5
   2.3 Rheology ............................................................................................................. 8
      2.3.1 Theory .......................................................................................................... 8
      2.3.2 Measuring Rheology .................................................................................... 9
      2.3.3 The Meaning of Workability ....................................................................... 10
   2.4 Hydrating Cement Systems .............................................................................. 12
      2.4.1 Portland Cement .......................................................................................... 13
         2.4.1.1 C₃S .......................................................................................................... 13
         2.4.1.2 C₂S .......................................................................................................... 14
         2.4.1.3 C₃A .......................................................................................................... 14
         2.4.1.4 C₄AF ...................................................................................................... 16
         2.4.1.5 Calcium Sulfates (i.e. Dihydrate, Hemihydrate and Anhydrite) .......... 16
         2.4.1.6 Alkalis .................................................................................................... 17
         2.4.1.7 Particle Size Distribution ...................................................................... 18
      2.4.2 Portland Cement Hydration .......................................................................... 19
         2.4.2.1 Initial Hydration ..................................................................................... 19
         2.4.2.2 Dormant Period ..................................................................................... 20
         2.4.2.3 Acceleration Period ................................................................................ 20
         2.4.2.4 Deceleration Period ................................................................................ 20
      2.4.3 The Importance of Adequate Sulfate Concentration .................................... 20
         2.4.3.1 Rheological Model .................................................................................. 20
         2.4.3.2 Influence of Temperature ...................................................................... 22
   2.5 Superplasticizers ................................................................................................. 23
## 2.6 Cement-Superplasticizer Interactions ........................................25

2.6.1 Introduction...............................................................................25
2.6.2 Superplasticizer Adsorption and Repulsion at the Cement-Solution Interface....26
2.6.3 Preferential Adsorption on Specific Surface Sites.................................28
2.6.4 Complexation and Solubilization of Ionic Species .................................33
2.6.5 Alteration of Hydration Rate and Hydration Products ..............................34
2.6.6 Influence of Temperature......................................................................35

## 2.7 Concluding Remarks ......................................................................36

### 3 Experimental ..................................................................................37

3.1 Investigation Techniques........................................................................37

3.1.1 Rotational Viscometer.........................................................................37
  3.1.1.1 Cement Paste and Mortar Experiments........................................37
  3.1.1.2 Concrete Experiments.................................................................39
3.1.2 Ion Chromatography (IC)....................................................................40
3.1.3 Total Carbon Analyzer (TOC)..............................................................40
  3.1.3.1 Instrumental Setup........................................................................40
  3.1.3.2 Definition of Superplasticizer Contents.........................................41
3.1.4 Atomic Absorption Spectrometer (AAS)...............................................42
3.1.5 Differential Scanning Calorimeter (DSC)...............................................42
3.1.6 Calorimetry.........................................................................................42
3.1.7 Characterization of Cement.................................................................42

3.2 Procedures..........................................................................................45

3.2.1 Preparation of Cement Paste and Mortar.............................................45
3.2.2 Preparation of Concrete......................................................................46
3.2.3 Preparation of Pore Water....................................................................46
3.2.4 Stopping of Cement Hydration............................................................46
3.2.5 Preparation for Powder Diffractometry (XRD).....................................46
3.2.6 Measuring Accuracy............................................................................47

3.3 Materials............................................................................................49

3.3.1 Cements ..........................................................................................49
3.3.2 Superplasticizers.................................................................................51
3.3.3 Other Materials..................................................................................52
3.3.4 Comparison of Mortar and Concrete....................................................53

### 4 Results ............................................................................................55

4.1 Pore Water Analysis............................................................................55
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1.1</td>
<td>Superplasticizer Concentration in Pore Water</td>
<td>56</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Ion Concentration in Pore Water</td>
<td>60</td>
</tr>
<tr>
<td>4.2</td>
<td>Rheological Analysis of Cement Paste and Mortar</td>
<td>62</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Tests Without Superplasticizers</td>
<td>62</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Influence of Superplasticizers on Rheological Parameters</td>
<td>65</td>
</tr>
<tr>
<td>4.2.2.1</td>
<td>Relative Yield Value</td>
<td>65</td>
</tr>
<tr>
<td>4.2.2.2</td>
<td>Relative Viscosity Coefficient</td>
<td>70</td>
</tr>
<tr>
<td>4.2.2.3</td>
<td>Stiffening Value</td>
<td>71</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Special Aspects</td>
<td>72</td>
</tr>
<tr>
<td>4.2.3.1</td>
<td>Delayed Superplasticizer Addition</td>
<td>72</td>
</tr>
<tr>
<td>4.2.3.2</td>
<td>Superplasticizer Dosage and Addition of Na$_2$SO$_4$</td>
<td>73</td>
</tr>
<tr>
<td>4.2.3.3</td>
<td>Influence of W/C Ratio</td>
<td>74</td>
</tr>
<tr>
<td>4.2.3.4</td>
<td>Addition of Other Inorganic Salts</td>
<td>75</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Comparison of Mortar and Concrete</td>
<td>77</td>
</tr>
<tr>
<td>4.3</td>
<td>Hydrates</td>
<td>80</td>
</tr>
<tr>
<td>4.4</td>
<td>Heat of Hydration</td>
<td>82</td>
</tr>
<tr>
<td>4.5</td>
<td>Summary of Results</td>
<td>84</td>
</tr>
<tr>
<td>5</td>
<td>Discussion</td>
<td>87</td>
</tr>
<tr>
<td>5.1</td>
<td>Cement Composition</td>
<td>87</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Sulfates</td>
<td>87</td>
</tr>
<tr>
<td>5.1.1.1</td>
<td>Origin of Sulfates</td>
<td>88</td>
</tr>
<tr>
<td>5.1.1.2</td>
<td>Quantity of SO$_4^{2-}$ Dissolved in the Pore Water</td>
<td>89</td>
</tr>
<tr>
<td>5.1.1.3</td>
<td>Hydrates Detected by DSC</td>
<td>90</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Influence of Cement Composition on the Rheological Behavior</td>
<td>91</td>
</tr>
<tr>
<td>5.1.2.1</td>
<td>Cement Phase Composition and Rheological Behavior</td>
<td>91</td>
</tr>
<tr>
<td>5.1.2.2</td>
<td>Heat Evolution and Rheological Behavior</td>
<td>96</td>
</tr>
<tr>
<td>5.2</td>
<td>Cement-Superplasticizer Interactions</td>
<td>98</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Superplasticizer Adsorption and Fluidity</td>
<td>98</td>
</tr>
<tr>
<td>5.2.1.1</td>
<td>Superplasticizer Adsorption on Cement Particles</td>
<td>98</td>
</tr>
<tr>
<td>5.2.1.2</td>
<td>Influence of Initial Cement Hydration on Superplasticizer Adsorption</td>
<td>100</td>
</tr>
<tr>
<td>5.2.1.3</td>
<td>Influence of Sulfate Ion Concentration on Relative Yield Value</td>
<td>101</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Rheological Model Based on Superplasticizer Adsorption Behavior and Sulfate Ion Content</td>
<td>103</td>
</tr>
<tr>
<td>5.2.3</td>
<td>Relative Yield Value at Different Temperatures</td>
<td>105</td>
</tr>
<tr>
<td>5.2.3.1</td>
<td>Cements A, C, D, and E</td>
<td>105</td>
</tr>
<tr>
<td>5.2.3.2</td>
<td>Cement B</td>
<td>110</td>
</tr>
<tr>
<td>5.2.4</td>
<td>Limits of the Model</td>
<td>111</td>
</tr>
</tbody>
</table>
ABBREVIATIONS / GLOSSARY

Cement nomenclature

C: Calcium oxide (CaO)
S: Silicon dioxide (SiO₂)
A: Aluminum oxide (Al₂O₃)
F: Iron trioxide (Fe₂O₃)
H: Water (H₂O)
C₃S: Tricalcium silicate ("Alite")
C₂S: Dicalcium silicate ("Belite")
C₃A: Tricalcium aluminate
C₄AF: Tetracalcium ferroaluminate
CsH₂: Gypsum, CaSO₄·2H₂O
CH: Portlandite, Ca(OH)₂
DH: Calcium sulfate dihydrate, CaSO₄·2H₂O
HH: Calcium sulfate hemihydrate, CaSO₄·0.5H₂O
AH: Anhydrite, CaSO₄

Other shortenings

(Q)XRD: (Quantitative) X-ray diffraction
DSC: Differential scanning calorimetry
AAS: Atom adsorption spectroscopy
IC: Ion chromatography
TOC: Total organic carbon (Corg)
Glossary of terms

Agglomerated particles form of a network-like structure, in which the particles are stuck together. Dispersed particles do not stick together.

Direct superplasticizer addition means that the superplasticizer is added to the mixing water. A superplasticizer addition some minutes after the start of the cement hydration is called delayed superplasticizer addition.

False set: the rapid development of rigidity in a mixed Portland cement suspension. This rigidity can be dispelled and fluidity regained by further mixing without addition of water.

Flash set: the rapid development of rigidity in a mixed Portland cement paste, mortar or concrete usually with the evolution of considerable heat. Rigidity cannot be dispelled nor can the fluidity be regained by further mixing without addition of water.

Fluidity: a subjective term, which defines the flow behavior of a cement paste or a concrete. If the fluidity is high, the cement paste or the concrete flows easily. Fluidity measurements are performed by various kinds of tests (e.g. mini-slump test, ordinary slump test, slump flow test, funnel test, etc.).

Gypsum: often used as an umbrella term for calcium sulfates, which are added as set retarders to cement clinker.

Interstitial phase: molten part during the clinker manufacture process consisting of C₃A, C₄AF and minor cement phases.

Ionic strength: the weight concentration of ions in the pore water, computed by multiplying the concentration of each ion in the pore water (C) by the corresponding square of the charge on the ion (z) summing this product for all ions in the pore water and dividing by 2 (Ι = 0.5Σ(z² × C)).

Secondary gypsum: Precipitates during the initial hydration reactions due to oversaturated conditions.

Slump flow/slump spread/mortar flow: horizontal spread of the concrete or mortar, after the slump cone has been lift up; normally expressed as diameter or area.

Viscous: the tendency of a liquid to resist flow as a result of internal friction.

w/c ratio: water to cement ratio.

Workability: how easily fresh concrete can be placed and consolidated in forms.
In dieser Arbeit wurde das rheologische Verhalten (d.h. das Fliessverhalten) von drei Hochleistungsbetonverflüssigern (HBV: Polymelaminsulfonat, Polynaphthalensulfonat, Polyacrylat) in Kombination mit verschiedenen Zementen (CEM I 42.5) aus der Schweiz eingehend untersucht. Ziel war es, die Wechselwirkungen zwischen Zement und Hochleistungsbetonverflüssiger zu bestimmen, sowie die wichtigsten Parameter zu ermitteln, die das rheologische Verhalten während der ersten zwei Stunden beeinflussen. Während dieser Zeit wird Beton üblicherweise angemacht, transportiert und eingebaut. Die rheologischen Untersuchungen an Zementleim, Mörtel und Beton wurden durch XRD, Porenwasseranalysen, Hydratationswärmemessungen und DSC-Messungen ergänzt.


Als wichtigste Parameter ergaben sich folgende Kenngrössen:

- Gehalt an $C_3A$
- Gehalt an wasserlöslichen Alkalien ($Na^+$, $K^+$)
- HBV-Art und -Dosierung
- Mörtel- resp. Zementleimtemperatur
- W/Z-Wert
Der Einfluss der Temperatur ist in der Literatur bis anhin kaum beschrieben worden, obwohl in der Praxis die Frischbetontemperatur ohne weiteres zwischen 5 und 30°C variieren kann.

Der Gehalt an C₃A und an wasserlöslichen Alkalien hängt vom Zement ab. Für die untersuchten Zemente variierten diese Werte von 1.5 bis 12 Gew.-% C₃A, sowie von 0.22 bis 0.96 Gew.-% Na₂O-eqsol. Der Einfluss dieser Parameter kann nur an unterschiedlichen Zementen verglichen werden oder muss durch Zugabe ähnlicher Stoffe simuliert werden. Eine solche Simulation erfolgte für den Gehalt an wasserlöslichen Alkalien durch Zugabe von Na₂SO₄ zum Anmachwasser.

Porenwasseranalysen haben gezeigt, dass die Menge an adsorbiertem und eingebautem HBV stark vom C₃A-Gehalt eines Zementes abhängt. Zudem ist diese Menge bei gleicher HBV-Konzentration bei den drei untersuchten HBV unterschiedlich. Beim Polyacrylat war sie am kleinsten, beim Polynaphthalensulfonat am größten. Eine Zugabe von Na₂SO₄ zum Anmachwasser erhöhte den Anteil an HBV, welcher im Porenwasser verbleibt, d.h. welcher nicht adsorbierter oder eingebaut wurde.


Der Einfluss der Temperatur auf HBV-enthaltende Mörtel ist sehr variabel und nicht vergleichbar mit Systemen ohne HBV. Trotzdem konnten die Temperaturcharakteristiken der relativen Fliesswiderstände von 4 der 5 untersuchten Zemente (Zement A, C, D, E) mit dem oben erwähnten HBV-Adsorptionsmodell erklärt werden. Ein Zement-HBV-System bewegte sich mit steigender Temperatur entweder in Richtung Überdosierung oder Unterdosierung. Diese Verschiebung scheint lediglich vom Zement abhängig zu sein. Sie erfolgte unabhängig vom verwendeten HBV.

Abschließend werden die aus der Arbeit gewonnenen, praxisrelevanten Hinweise zusammengestellt und ein Ausblick auf weiterführende Untersuchungen gegeben.
ABSTRACT

In this work the rheological behavior (i.e. the flow behavior) of three superplasticizers (polymelamine sulfonate, polynaphthalene sulfonate, polyacrylate) in combination with various Swiss cements (CEM I 42.5) was studied intensively. The aim was on the one hand to determine the interactions between cements and superplasticizers and on the other hand to determine the most important parameters, which influence the rheological behavior during the first two hours of cement hydration. During this time concrete is usually mixed, transported, and placed. The rheological investigations on cement paste, mortar and concrete were completed by XRD, pore water analyses, heat of hydration and DSC-measurements.

The hydration of cement contains many reactions, which mainly depend on the cement composition, the w/c ratio, and on temperature. Both the flow behavior of mortar and concrete at the beginning of the hydration, and the hardening of the cement (or the concrete) are decisively influenced by these hydration reactions. Nowadays, various chemical additives are used, which deliberately or non-deliberately alter the hydration process. Due to the complexity of the ongoing hydration reactions and due to the insufficient knowledge, it is not always possible to alter the hydration behavior as requested.

The most important parameters turned out to be:

- the amount of C₃A
- the water-soluble alkalis (Na⁺, K⁺)
- the type and amount of superplasticizer used
- the mortar or cement paste temperature
- the w/c ratio

To date, the influence of temperature has hardly been described. However, in practice, concrete temperature may easily vary from 5 to 30°C.
The content of $C_3A$ and water-soluble alkalis depends on the cement. For the investigated cements these contents vary from 1.5 to 12.6 wt.-% $C_3A$, and from 0.22 to 0.96 wt.-% $Na_2O$-eq$_{sol}$. The influence of these two parameters can only be compared with different cements or simulated by the addition of similar materials. This kind of simulation was done for the water-soluble alkalis by adding $Na_2SO_4$ to the mixing water.

**Pore water analyses** showed that the amount of adsorbed and incorporated superplasticizer strongly depends on the $C_3A$ content of the cement. Moreover, this amount was different at equal superplasticizer dosages for the three superplasticizers under study. For the PC superplasticizer it was lowest, whereas for the PNS superplasticizer it was highest. The addition of $Na_2SO_4$ to the mixing water increased the fraction, which remained in the pore water, i.e. which was not adsorbed or incorporated.

It was shown that the content of $SO_3$ in the clinker correlates with the water-soluble alkali content ($r^2=0.81$). It follows that the content of $SO_3$ in the clinker mainly derives from easily soluble alkali sulfates. Moreover, it was shown that during the first 30 minutes water-soluble alkalis get dissolved by more than 50% and 66% having w/c ratios of 0.35 and 50, respectively. At this time only some percent of the cement has been hydrated. In order to reach such a high dissolved amount, alkali sulfates preferentially have to be monomineralic and/or they preferentially have to occur at the surface of the polymineralic cement particles. These findings corroborate that besides the addition of calcium sulfates as set retarders, water-soluble alkalis are very important sulfate ion suppliers, especially at low w/c ratios. This is especially important for the understanding of cement-superplasticizer interactions, since sulfate ions and $C_3A$ are mainly responsible for the adsorption behavior of superplasticizers.

**The rheological investigations** on cement paste and mortar were performed with a rotational viscometer at constant mortar temperatures (8, 20, 30°C). Thus, the influence of cement paste and mortar temperature on the flow behavior could be investigated. Within the measuring range of the viscometer, the cement suspensions behaved like Bingham-fluids. From the three investigated parameters (relative yield value, relative viscosity coefficient and stiffening value) relative yield value was found to be the most suitable parameter to predict the flow behavior. Without the use of superplasticizers, relative yield value increased with increasing temperature. A possible explanation for this behavior could be the ettringite content, which increased for the investigated samples from 10 to 30°C.

Without the use of superplasticizer the relative yield value of the 10 cements under study was linearly correlated with the product of $C_3A$ times cement fineness ($r^2=0.65$). If the $C_2S$ content was further considered, the correlation coefficient increased to 0.74. For superplasticized mortars the quality of the correlation depended on the superplasticizer dosage. Besides the product of $C_3A$ times cement fineness, no other
The parameter could be found. The C_{2}S content did not have any influence on the correlation coefficient.

By increasing the superplasticizer content the relative yield value decreases. The fluidifying effect of the PC superplasticizer was most pronounced. The impact of Na_{2}SO_{4} addition to the mixing water of superplasticized concrete depended on the investigated systems (i.e. cement-superplasticizer-temperature). It can generally be assumed that the relative yield value has a minimal value at an appointed Na_{2}SO_{4} content (parabolic curve). At higher or lower contents of Na_{2}SO_{4} the amount is not optimized with respect to relative yield value (concept of the over- and underdosed state with regard to Na_{2}SO_{4} addition). The optimal Na_{2}SO_{4} content can significantly be shifted depending on the superplasticizer and cement used as well as on the mortar temperature applied. It is thus possible that with an increasing amount of Na_{2}SO_{4} only the increasing part of the parabolic curve is measured.

The influence of Na_{2}SO_{4} addition on the relative yield value could be explained on the basis of a superplasticizer adsorption model. Thereby, fluidity is determined by the amount of superplasticizer adsorbed at the cement particle surface. This amount is influenced by the C_{3}A content of cement, by the superplasticizer molecules incorporated in the hydrates, and by the content of sulfate ions in the pore water.

The influence of temperature on superplasticized mortars was very variable and not comparable to systems without superplasticizer. Nevertheless, the temperature characteristics of the relative yield value from 4 of the 5 investigated cements (Cement A, C, D, E) could be explained by the above-mentioned superplasticizer adsorption model, except for cement B. With increasing temperature a cement-superplasticizer system is changing either into the direction of the underdosed state or into the overdosed one. It seems that the direction of this shift only depends on the cement used. It is independent from the superplasticizer used.

Finally, recommendations of practical interest as well as an outlook on continuative investigations are given.
1 INTRODUCTION

1.1 General Overview

The hydration of cement proceeds in a very complex manner. Even today the mechanisms of cement hydration are not fully understood. Superplasticizers are chemical admixtures, which are used in construction industry to specifically alter the flow behavior and the mechanical properties of concrete [1]. Therefore, it does not surprise that superplasticizers also alter the hydration behavior of the phases present in a cement. These so-called "cement-superplasticizer interactions" may be visualized by many analyzing techniques (i.e. fluidity evolution, strength development, phase analysis, pore water analysis, heat of hydration, etc.). However, the linking up of results from a microscopical view (i.e. pore water analysis) with the macroscopic outcome (i.e. fluidity of mortar or concrete) is not always possible.

It has been shown that superplasticizers are incorporated into the initial hydration products [2]. This incorporation has a negative effect to dispersion, since less superplasticizer is present to disperse the cement particles. Moreover, various superplasticizers were found to be differently adsorbed by the same cement [3, 4]. When using a superplasticizer, C₃A and C₄AF exert the highest affinity to adsorb superplasticizers. As C₃A is the cement phase that hydrates the most quickly within the very first minutes of cement hydration, it is the phase, which is most important for cement-superplasticizer interactions. In fact, pore water analysis showed that cements rich in C₃A consume a large amount of the added superplasticizer polymers within the first minutes of cement hydration [5].

Superplasticizer adsorption behavior is also influenced by the content of sulfates ions in the pore water [6, 7]. This content is hardly assessable, since sulfate ions originate from various sources. Moreover, sulfate ions are further consumed by hydration reactions.

At construction sites the consistency of concrete is usually measured in terms of a simple test like the slump or the slump flow test. Rheological tests made with more scientific test devices
are scarce. Due to climatic conditions, concrete temperature may vary significantly within a few days [8]. In a laboratory, rheological tests are usually performed at room temperature by simple test devices. Quite often, mortar or cement paste is used instead of concrete in order to minimize costs and time. Due to this simplification the question arises, whether such results are also valid for concrete.

1.2 Thesis Objectives

The scope of the present work is to investigate the various parameters influencing the rheological properties of freshly mixed ordinary Portland cement paste and mortar. The investigated cements should cover a broad range of CEM I 42.5 cements; additionally, it should be clarified, whether the results on mortar and cement paste are fully transferable to concrete.

From literature the following parameters were found to be of great importance:

- type and amount of superplasticizer
- composition of the cement (especially the contents of C$_3$A and soluble alkali sulfates as well as the fineness of the cement)
- temperature of the mixture

The rheological behavior of cement paste, mortar and concrete depends on the shear rate of a system. Hence, measuring instruments using variable shear rates (i.e. rotation speeds) have to be used in order understand and predict the rheological behavior.

Besides the macroscopical outcome of cement-superplasticizer interactions (i.e. rheological properties), it is necessary to combine the information of different analyzing techniques. Analyses of the pore water as well as the cement phase composition are needed to provide valuable information with regard to the rheological behavior. Particular attention is paid to the content of C$_3$A as well as to the origin and the role of soluble sulfate ions on the adsorption behavior of superplasticizers. The influence of soluble sulfate ions in the pore water is simulated by the addition of commercial alkali sulfates (i.e. Na$_2$SO$_4$) to the mixing water.

Another important goal of this work is to highlight the influence of temperature of cement-superplasticizer interactions. Up to now, most of the publications dealing with the consistency of superplasticized cements refer to experiments made at room temperature. Nevertheless, temperature has a pronounced effect on the hydration kinetics of cement and therefore a strong influence on the consistency. Hence, this parameter has to be investigated specifically.
Finally, a model should be developed, which is able to explain the results by means of the most important parameters and to predict the interactions between cements and superplasticizers. Thus, it should be possible to either forecast rheological incompatibilities or to solve them within reasonable time. For this reason a testing procedure is needed, which is able to describe and characterize the rheological behavior of superplasticized cement systems.
1. INTRODUCTION
2 LITERATURE

2.1 Introduction

The aim of this literature review is to describe the state of the knowledge of the interactions occurring in superplasticized cement systems during the first hours of cement hydration. Superplasticizers help to improve the flow behavior of concrete. By adding new components (i.e. chemical admixtures, fly ash, silica fume) to the cement-water-aggregate system, the entire system can be affected. This may be intensified for superplasticized concrete, since the water to cement ratio (w/c ratio) is generally lower compared to ordinary concrete. The first two sections of this review are dedicated to the forces acting between particles and to rheology (Chap. 2.2 and Chap. 2.3). The following sections contain information about cement chemistry (Chap. 2.4), the types of superplasticizers (Chap. 2.5), and the interactions between cements and superplasticizers (Chap. 2.6). Finally, some remarks conclude this review (Chap. 2.7).

2.2 Forces Affecting Small Particles

Grain size of cement and aggregates ranges from less than 1 µm to several centimeters. The stability of such a water-particle suspension is governed by various forces (e.g. gravitational forces, capillary forces, electrostatic forces/colloidal forces). The resulting forces mainly depend on the particle size of the components (Tab. 2-1).
The distance between two adjacent colloidal particles depends on the interaction potential \( V_{\text{int}} \), which is the sum of attractive (van der Waals) and repulsive forces (i.e. electrostatic forces) (Fig. 2-1). All colloids are either positively or negatively charged, while the overall charge in the suspension has to be zero. The particles might be charged either as a result of imperfections in the crystal structure near the surface, adsorption of specific ions on the surface, or dissolution of ionic species from the surface [9, 10]. Depending on the charge of the particles, a cementitious suspension can be in a dispersed or in a flocculated state. Flocculated particles may retain water, which is no longer available for the initial hydration reactions [11]. Because of the charge, particles having the same charge may not come close enough to agglomerate into larger particles in the primary minimum due to the separating effect of the energy barrier (Fig. 2-1). If the energy barrier is lower for instance at higher ionic strength of the aqueous solution or at lower particle charge, the particles may agglomerate irreversibly. The secondary minimum is thought to be important for cementitious systems, since this state of agglomeration (i.e. flocculation) is reversible and thus can be easily turned into the dispersed state.

The balance between charged colloids and other electrical species can be described by the "diffuse double layer theory" (Fig. 2-2): A charged particle is surrounded by a fixed layer of oppositely charged ions ("stern layer"). This layer is followed by a diffuse layer with a mixture of oppositely charged ions. The surface between the fixed and the diffuse layer is called the shear plane. Zeta potential is defined as the potential difference between the shear plane and the end of the diffuse layer. This potential is taken as an approximation of the surface charge of the particle, since it is not possible to measure the surface potential of the particle itself. Zeta potential is obtained by measuring charged particles in suspension and observing their mobility under an electric field gradient.

As cement particles in contact with water acquire an electronic charge, zeta potential is an important and useful parameter, which can be used to predict and control the stability of a cement suspension.

<table>
<thead>
<tr>
<th>Particle size [mm]</th>
<th>Type of particle</th>
<th>Kind of predominant force</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 1 mm</td>
<td>coarse sand, gravel</td>
<td>shear forces, gravity</td>
</tr>
<tr>
<td>0.1-1 mm</td>
<td>sand</td>
<td>capillary forces</td>
</tr>
<tr>
<td>10^{-6} - 0.1 mm</td>
<td>cement particles, hydrates, smallest particles</td>
<td>colloidal forces (i.e. electrostatic, van der Waal forces)</td>
</tr>
</tbody>
</table>

Tab. 2-1: Different kinds of forces in a water particle suspension [9].
Fig. 2-1: Forces acting between particles: Interaction potential ($V_{\text{int}}$) as a function of distance ($h$). The energy barrier impedes that two particles irreversibly agglomerate (primary minimum). The flocculation state in the secondary minimum is reversible [12].

Fig. 2-2: Electric double layer of a negatively charged particle. The potential difference between shear plane and the end of the diffuse layer is called the zeta potential [13].
2.3 Rheology

2.3.1 Theory

Rheology is defined as "the science of the deformation and flow of matter" [14]. Fluids are characterized by their flow curves, resulting from the relation between shear stress ($\tau$) and shear rate ($\gamma'$) under simple steady shear. The simplest behavior is the Newtonian fluid behavior, which has a linear correlation between shear stress and shear rate. The shear stress of this fluid (e.g. water) can be described by:

$$\tau = \eta \gamma'$$  \[2.1\]

where "$\tau$" is the shear stress, "$\eta$" the constant of proportionality, which is called the coefficient of viscosity, and "$\gamma'$" the shear rate. Only a single point is needed to determine this flow behavior (Fig. 2-3). However, most fluids are non-Newtonian fluids, which means that more than one point is needed to describe their flow behavior (Fig. 2-3). Cement paste, mortar and concrete can be described as viscoplastic suspensions. This means that below a critical stress value (i.e. the yield value) the material behaves like a solid but flows like a viscous liquid when this stress is exceeded ($\tau > \tau_o$) [14]. The simplest type of this behavior is the linear Bingham flow behavior (Fig. 2-3):

$$\tau = \tau_o + \mu \gamma'$$  \[2.2\]

where "$\tau_o$" is the yield value, "$\mu$" the plastic viscosity, which has the dimensions of viscosity [10], and "$\gamma'$" the shear rate. Plastic viscosity is the slope of the linear line of a Bingham fluid. In many cases the flow behavior of cement paste, mortar or concrete can be expressed by this formula. The yield value is a measure of the force necessary to start a movement of the concrete ("flow resistance"), whereas the plastic viscosity is a measure of the resistance of the concrete against an increased speed of movement [15].

However, fluids do not always exhibit a linear flow behavior. In such cases non-linear models like the model of Herschel-Buckley may be applied [14]:

$$\tau = \tau_o + k \gamma'^n$$  \[2.3\]

where "$\tau_o$" is the yield value, "$k$" and "$n$" constants and "$\gamma'$" the coefficient of viscosity.
2.3.2 Measuring Rheology

A rotating viscometer is the classical laboratory instrument for determining the flow behavior of non-Newtonian fluids. Today, there exist several so-called rheometers. Some are only designed for cement paste or mortar suspensions (Viscomat PC/NT, [16]), others for mortar and concrete (BTRHEOM, [17], IBB [18], BML [19], Two-point apparatus [20]). Their mode of action varies from type to type. A rotating impeller (IBB, Two-Point apparatus, Viscomat PC/NT), two parallel plates (BTRHEOM), or coaxial cylinders rotating against each other (BML) induce a torque, which is measured at various rotating speeds. It was shown that the relation between torque and rotation speed is mathematically identical to the Bingham flow behavior [10]:

\[ T = g + h \cdot R \]  

where "T" is the torque, "R" the rotation speed, "g" a measure of yield value \( (\tau_\sigma) \) and "h" a measure of plastic viscosity \( (\mu) \). This relationship is very useful, since it is not trivial to convert Eq. (2.4) into Eq. (2.2). For such a conversion, the three-dimensional shearing of the material has to be known as a function of the rotation velocity. For complicated testing geometries (e.g. mortar paddle of the rotational viscometer) this information is not available. Thus, depending on the geometric design of a rheometer, yield value and plastic viscosity can be expressed in relative (i.e. Nm, Nmm; Nm-s, Nmm-s) or in fundamental units (i.e. Pa, Pa-s).

Fig. 2-3: Different flow behaviors: a) Newtonian flow behavior, b) Bingham flow behavior, c) non-linear Herschel-Buckley flow behavior.
2.3.3 The Meaning of Workability

Workability is the property of freshly mixed concrete or mortar that determines the ease and partly the homogeneity, with which it can be mixed, placed, consolidated and finished [21]. It often contains personal impressions with regard to the ability of the concrete to be transported, pumped and placed, to flow and to segregate, to have a good consistency and stability. Although these are subjective terms differing from one observer to another, they are widely used in the concrete industry. The workability of a concrete mix is affected by its mix proportion (cement, aggregates, water), the chemical and physical properties of the cement, the physical properties of the aggregates (particle size, shape, water adsorption, surface texture), the presence, quantity and mode of introduction of admixtures, and the time of hydration [22]. In practice, there are several testing devices in order to measure workability like the slump (Fig. 2-4) or the slump flow test, the flow table test, the degree of compactability and many more. Mainly slump or slump flow tests are used.

![Fig. 2-4: Slump test according to SIA 162-1. After lifting the cone, the slump is measured. Slump flow values or similar measurements (e.g. mortar flow) are defined as a horizontal spread of the suspension, normally expressed as diameter or area.](image)

As already mentioned, the rheological behavior of fluids depends on the applied shear rate. In order to fix the line for the mathematical relation of a Bingham fluid, at least two points at different shear rates are necessary. The above-mentioned tests only describe the flow behavior at a constant shear rate. They are therefore called one-point tests, whereas tests measuring at different shear rates are called two-point tests. Values obtained from one-point tests should thus be used with care, because they do not fully characterize the flow behavior.

The general effect of various mix constituents on yield value and plastic viscosity is shown in Fig. 2-5 [23]. A good correlation has often been reported between yield value and slump or slump flow [10, 24, 25] (Fig. 2-6). This correlation is very important, since the slump test is widely used all over the world. In Fig. 2-7 the torque is plotted against the rotation speed. It is possible that two mixes may have the same slump (∼ i.e. same yield value, mix A and B)
but exhibit a different behavior at higher shear rates. On the other hand two mixes may behave similarly at an applied shear rate (mix B and C at 120 rpm), but the slump may be completely different. Plastic viscosity cannot easily be correlated to values of other measurements. Nevertheless, it is thought to be strongly influenced by the larger particles [24].

**Fig. 2-5:** The effect of water compared to that of superplasticizers (SP) and air-entraining admixtures (AE) on the rheological parameters plastic viscosity and yield value (adapted from [23]).

**Fig. 2-6:** Slump and slump flow vs. relative yield value. A fairly good correlation \((r^2=0.80-0.85)\) exists between yield value (measured with a BML rheometer), slump and slump flow of ordinary Portland concrete [25].
Rheometers give a better insight into the flow behavior of concretes. But usually they are not suitable outdoors due to their heavy weight and large size. Moreover, the use of rheometers takes more time compared to a simple one-point test. Therefore, they will not replace the existing techniques at jobsites for the next years. However, for optimizing the mix design of a concrete or mortar they are very helpful devices and provide valuable results.

2.4 Hydrating Cement Systems

Already the Egyptians used burnt gypsum mortars for their monumental constructions [26]. The Romans called their cementitious masonry work "opus caementitium". They used volcanic material, crushed clay bricks and lime as hydraulic material [27]. In 1824, Joseph Aspdin of England took out a patent on the product "Portland cement". This cement was burned at a well-defined ratio of finely ground limestone and clay. The product was then ground and yielded good hydraulic properties. Today, cement is an irreplaceable building and construction material and its raw material still consists of limestone and clay. Due to economical and ecological reasons, alternative materials (e.g. fly ash, slag) may partly replace clinker raw materials and the cement itself without reducing the technically desired properties [28].

**Fig. 2-7:** Flow behavior of different hypothetical mortar mixes. Although the slump values may be identical for mix A and B (since slump correlates with yield value), relative viscosity coefficient is not. Mix B and C exhibit the same torque at 120 rpm, but show a completely different yield value at zero rpm.
2.4.1 Portland Cement

Cement production involves the heating, calcining\(^1\) and sintering\(^2\) of ground raw materials, typically limestone and clay. In order to produce the technically desired hydraulic cement phases, the raw material mixture has to be within a well-defined range of calcium, silicon, iron, and aluminum oxide. At around 1450 °C the material consists of a molten interstitial phase, which will mainly yield C\(_3\)A and C\(_4\)AF, and of the sintered solid phases C\(_3\)S and C\(_2\)S. The material is then cooled down very fast, so that the clinker solidifies in this equilibrium composition. Afterwards, the clinker is ground with a small amount of gypsum in order to give Portland cement.

Portland cement clinker consists of the four main phases C\(_3\)S, C\(_2\)S, C\(_3\)A and C\(_4\)AF, and of minor phases. Due to the industrial process, these phases are not pure phases but contain variable amounts of foreign ions in their crystal lattice, which may alter the crystal structure. A list of the characteristics of the four cement main phases is given in Tab. 2-2.

### 2.4.1.1 C\(_3\)S

C\(_3\)S is essential for the hardening of concrete. There are several crystal modifications of C\(_3\)S, but the reactivity does not change very much [26]. When added to water, different ions are immediately dissolved from the grain surface (H\(_2\)SiO\(_4\)\(^2-\), OH\(^-\), Ca\(^{2+}\)). The hydration of C\(_3\)S generates two forms of hydrates, portlandite and the CSH-phases according to:

\[
\text{Ca}_3\text{SiO}_4 + 3\text{H}_2\text{O} \rightarrow 3\text{Ca(OH)}_2 + \text{SiO}_2\text{H}_4\text{O}_4\]

---

1. In the calcining phase, limestone is converted into lime, releasing carbon dioxide (CaCO\(_3\) -> CaO + CO\(_2\)).
2. Sintering is the process, in which fine particles of a material become chemically bonded at a temperature that is sufficient for atomic diffusion. Chemically, the calcium oxide produced in the first stage reacts with silicon dioxide and alumina- and iron-bearing compounds to form C\(_3\)S and C\(_2\)S plus lesser quantities of C\(_3\)A, C\(_4\)AF, and several other compounds.

---

<table>
<thead>
<tr>
<th>Parameter</th>
<th>C(_3)S</th>
<th>C(_2)S</th>
<th>C(_3)A</th>
<th>C(_4)AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount in CEM I</td>
<td>40-80</td>
<td>0-30</td>
<td>3-15</td>
<td>4-15</td>
</tr>
<tr>
<td>Reactivity</td>
<td>high</td>
<td>low</td>
<td>very high</td>
<td>low</td>
</tr>
<tr>
<td>Impurities</td>
<td>Al(_2)O(_3), Fe(_2)O(_3), MgO</td>
<td>Al(_2)O(_3), Fe(_2)O(_3), Na(_2)O, K(_2)O, SO(_3)</td>
<td>Fe(_2)O(_3), Na(_2)O, K(_2)O, (MgO),</td>
<td>MgO, SiO(_2), TiO(_2)</td>
</tr>
<tr>
<td>Technical name</td>
<td>alite</td>
<td>belite</td>
<td>alinate phase</td>
<td>ferrite phase</td>
</tr>
<tr>
<td>Heat of hydration [J/g]</td>
<td>500</td>
<td>250</td>
<td>1340</td>
<td>420</td>
</tr>
<tr>
<td>Contribution to strength</td>
<td>high at early ages</td>
<td>high at late ages</td>
<td>high at very early ages</td>
<td>very low</td>
</tr>
</tbody>
</table>

Tab. 2-2: Main phases of Portland cement and their characteristics [26, 29].
2. LITERATURE

2.4.1.2 C₃S

There are five different crystal modifications of C₃S, while the ß-modification is the most common [30]. The hydration products of C₃S are mainly the same as for C₃S, while the rate of hydration is much slower:

\[ 2 \text{C}_2\text{S} + 4 \text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 \text{ (CSH)} + \text{CH} \text{ (portlandite)} \]  \[2.6\]

2.4.1.3 C₃A

The hydration of C₃A is very important for the rheological behavior during the first hours of cement hydration. The hydration is very much influenced by the presence of gypsum. Without gypsum the initial hydration reaction is very quick, which immediately leads to a stiff consistency. C₃A is firstly converted into unstable phases, further into the stable calcium aluminate hydrate phase (C₃A₆₃), which has a platy hexagonal shape of about 10 \( \mu \text{m} \) in size [29]:

\[ 2 \text{C}_3\text{A} + 21 \text{H} \rightarrow \text{C}_4\text{A}_1\text{H}_{13} \text{ (unstable)} + \text{C}_2\text{A}_8 \text{ (unstable)} \]  \[2.7\]

\[ \text{C}_4\text{A}_1\text{H}_{13} + \text{C}_2\text{A}_8 \rightarrow 2 \text{C}_3\text{A}_6 \text{ (stable)} + 15 \text{H} \]  \[2.8\]

The addition of gypsum makes concrete placeable. In the presence of its dissolved components Ca²⁺ and SO₄²⁻, C₃A is converted into ettringite, which is a calcium aluminate trisulfate (Fig. 2-8a):

\[ \text{C}_3\text{A} + 3 \text{Ca}^{2+} + 3 \text{SO}_4^{2-} + 32 \text{H} \rightarrow \text{C}_3\text{A·3Cs·H}_{32} \text{ (ettringite)} \]  \[2.9\]

Ettringite has a fibrous morphology consisting of long hexagonal needles. The length of the needles strongly depends on the environmental conditions. This hydrate phase is formed around the C₃A containing grains and protects them from further rapid hydration during the dormant period (Chap. 2.4.2). However, fast initial ettringite crystallization may also be the cause of false setting [31]. During the deceleration period (Chap. 2.4.2.4) ettringite gets unstable due to an insufficient sulfate ion supply. It is converted into calcium aluminate monosulfate (monosulfate, Fig. 2-8b):

\[ \text{C}_3\text{A·3Cs·H}_{32} + 2 \text{C}_3\text{A} + 4 \text{H} \rightarrow 3 \text{C}_3\text{A·Cs·H}_{12} \text{ (monosulfate)} \]  \[2.10\]
This phase has a hexagonal, platy shape of about 50 µm in diameter. In the presence of carbonate ions (e.g. from limestone fillers), carbonate containing phases can occur instead of monosulfate.

Pure C₃A has a cubic crystal modification. By increasing the amount of entrapped alkali ions, the crystal structure is altered from the cubic to the orthorhombic and further to the monoclinic modification [32, 33]. In commercial available cements only the cubic and the orthorhombic modification have been found [34]. The crystal modification also depends on the burning and cooling history during the cement manufacture process [35, 36].

There are various statements in literature regarding the reactivity of C₃A modifications. Some researchers found doping C₃A with alkalis to decrease the reactivity [33, 37, 38], while others found the opposite [39]. Richartz and Adams found C₃A doped with K₂O to lead to a higher reactivity compared to the pure phase [40, 41]. Odler found Na₂O to reduce, K₂O to increase the hydration of C₃A [32]. He related the findings to the crystal lattice distortion due to the different ionic radii of Na⁺ and K⁺, since Na⁺ has a smaller and K⁺ a larger radius compared to the ions they are replacing. The hydration rate of C₃A may also be altered by the alkali sulfates dissolved in the pore water. The higher the alkali content in the pore water, the larger the amount of C₃A dissolution and ettringite production [42].

An important fact for rheological considerations is that only a part of the C₃A content is converted into ettringite during the first minutes of cement hydration. Depending on the reactivity, about 5 to 16 wt.-% of the total amount of C₃A is consumed during the first hour of cement hydration at room temperature [32, 43-45]. For a total conversion of C₃A into ettringite a cement with 10 wt.-% of C₃A would require about 9 wt.-% SO₃. This amount is not present in cements [46].
2.4.1.4 C₄AF

Depending on the composition of the raw material, C₄AF is a solid solution between the end members C₂F and C₃A [30]. The hydration of C₄AF is very much slower compared to C₃A, but the reactions may be written analogous:

without gypsum: \( \text{C}_4\text{AF} + 13 \text{ H} \rightarrow \text{C}_4(\text{A,F})\text{H}_{13} \) \[2.11\]

with gypsum: \( \text{C}_4\text{AF} + \text{CsH}_2 + 12 \text{ H} \rightarrow \text{C}_4(\text{A,F})\text{CsH}_{12} \) \[2.12\]

2.4.1.5 Calcium Sulfates (i.e. Dihydrate, Hemihydrate and Anhydrite)

Gypsum is added to the clinker in order to retard the intense initial hydration reactions. There are two stable natural forms of calcium sulfates, calcium sulfate dihydrate (dihydrate, \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)) and the water-free anhydrite (\( \text{CaSO}_4 \)). Calcium sulfate hemihydrate (\( \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} \)) is more soluble compared to the former phases and originates from the dehydration of dihydrate during the grinding process of the clinker at temperatures above 80°C [45, 48]. As decomposition proceeds, soluble anhydrite (anhydrite II) may occur in mills at temperatures above 100°C. Soluble anhydrite is as soluble as hemihydrate [48-50]. In a clinker itself, anhydrite may only occur, if the quantity of clinker sulfate is higher compared to the amount that can be incorporated into alkali sulfates and other cement phases [51]. Anhydrite has been detected at a very high sulfate/alkali ratio of 3.6. In commercial cements such a high ratio rarely exists.

Fig. 2-8: Ettringite a) and monosulfate b) in cement. The hexagonal, platy crystals of monosulfate impede the fluidity much more compared to the elongated ettringite needles [47].
In contact with water the better soluble calcium sulfates (hemihydrate, soluble anhydrite II) enrich the pore water with sulfate and calcium ions. If the solubility product of gypsum is exceeded, secondary gypsum (i.e. dihydrate) precipitates.

The solubility of hemihydrate decreases with increasing temperature, as can be seen in (Fig. 2-9). The other types of calcium sulfates show less considerable temperature dependencies, while natural anhydrite is less soluble than dihydrate. Amathieu showed that different ions in the pore water could greatly affect the solubility of dihydrate and hemihydrate [52].

\[ \text{Sulfatisation degree (SD)} = \frac{100 \cdot \text{SO}_3 \times 0.774}{0.658 \cdot \text{K}_2\text{O} + \text{Na}_2\text{O}} \% \]  

where \( \text{SO}_3, \text{K}_2\text{O}, \text{Na}_2\text{O} \) are expressed as wt.-\% of cement. If there is a lack of sulfates (SD < 100), the alkalis are incorporated into other clinker phases like C_3A and C_2S. If there is
an excess of sulfates (SD >100), the remaining sulfates are incorporated into other clinker phases like C₃S [33, 58]. Therefore, the alkali containing modifications of C₃A should only occur at low sulfatisation degrees [58].

The solubility of alkali sulfates is generally higher than the one of calcium sulfates (Tab. 2-3). Thus, Portland cements may have the same total SO₃ content, but depending on the type of sulfate, the sulfate ion availability can be completely different.

Five different types of alkali sulfates are cited in literature to be present in cement: arcanite (K₂SO₄), aphthitalite (Na₂SO₄·3K₂SO₄), Ca-langbeinite (CaSO₄·K₂SO₄), thenardite (Na₂SO₄) and syngenite (CaK₂(SO₄)₂·H₂O) [47, 51, 57]. Their appearance is supposed to be a function of the sulfate content. At a low SO₃/alkali ratio arcanite and aphthitalite coexist, at higher ratios Ca-langbeinite replaces them [51]. Ca-langbeinite is thought to be the best phase with regard to rheology, because it provides both calcium and sulfates ions and helps to form a blocking ettringite layer around the C₃A. Therefore, it prevents further hydration [59, 60]. Syngenite was found to be favoured in cement pastes with high potassium contents (approx. >1 wt.-%) [40, 60, 61] or in cements with a high content of C₃A (>12 wt.-%) [33].

<table>
<thead>
<tr>
<th>Cement phase</th>
<th>Solubility (g/l) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydrate (CaSO₄·2H₂O)</td>
<td>2.1</td>
</tr>
<tr>
<td>Hemihydrate (CaSO₄·0.5H₂O)</td>
<td>6.2-8.2</td>
</tr>
<tr>
<td>Natural anhydrite (CaSO₄)</td>
<td>2.7</td>
</tr>
<tr>
<td>Soluble anhydrite (CaSO₄)</td>
<td>6.3</td>
</tr>
<tr>
<td>Arcanite (K₂SO₄)</td>
<td>120</td>
</tr>
<tr>
<td>Aphthitalite (Na₂SO₄·3K₂SO₄)</td>
<td>120</td>
</tr>
<tr>
<td>Calcium langbeinite (2CaSO₄·K₂SO₄)</td>
<td>6.3</td>
</tr>
<tr>
<td>Syngenite (CaSO₄·K₂SO₄·H₂O)</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Tab. 2-3: Solubility at room temperature of various sulfate sources in Portland cement [62].

2.4.1.7 Particle Size Distribution

Cements with low C₃A contents and low cement fineness were found to yield a higher fluidity compared to cements with high C₃A contents and high cement fineness [5]. However, the effect of cement fineness on the rheological properties is not always uniform. Although a higher fineness increases the reactivity of cement, there might be a fluidifying effect due to a better particle size distribution (i.e. filling effect) and a lower water consumption. These
effects have been observed by the addition of very fine aggregates (i.e. ultra fine fly ash, silica fume, limestone powder) to the cement [63-69].

2.4.2 Portland Cement Hydration

Immediately after the first contact of cement with water various reactions occur. These reactions may be visualized by measuring the heat flow as a function of time. Four stages can be identified [70, 71] (Fig. 2-10): an initial hydration period, a dormant period, an acceleration and a deceleration period. With respect to freshly mixed cement or concrete, only the initial hydration and the dormant period are important.

![Fig. 2-10: The four hydration stages of Portland cement hydration: initial hydration (called peak I), dormant period, acceleration and deceleration period. Sometimes a shoulder (conversion of ettringite (E) to monosulfate (M)) is visible at the deceleration period.](image)

2.4.2.1 Initial Hydration

As soon as hygroscopic cement comes into contact with water, easily soluble components like alkalis, calcium sulfate phases and free lime are dissolved by the surrounding water [44]. Na\(^+\), K\(^+\), Ca\(^{2+}\), SO\(_4\)\(^{2-}\) and OH\(^-\) ions are enriched in the pore water. Meanwhile, Ca\(^{2+}\) and H\(_2\)SiO\(_4\)\(^{2-}\) ions are hydrolyzed from the most reactive cement particles, particularly from C\(_3\)A and C\(_3\)S. Ettringite is formed around the C\(_3\)A containing surfaces. From the viewpoint of rheology, this reaction is the most important one. The initial C\(_3\)A dissolution may be increased by dissolved alkalis [42]. Besides ettringite, a small amount (1-5 wt.-\%) of calcium silicate hydrate (CSH) gel is formed around the C\(_3\)S containing cement grains [30]. Secondary gypsum may precipitate from the supersaturated pore water. After some minutes the cement grains are coated with a protective layer of hydration products. At this stage the reactions stop and the heat flux drastically decreases.
2.4.2.2 Dormant Period

The dormant period usually lasts several hours. During this time the concrete has to be transported and placed. This period is characterized by a very low heat flow. Nevertheless, the surface gel layer (CSH-phases) on the cement grains is thickening and the ettringite needles are slightly growing [70].

2.4.2.3 Acceleration Period

Several effects have been considered to explain the start of the acceleration period: disruption of the protective hydrates layer, nucleation and growth of CSH-phases or portlandite, recrystallization of ettringite [31, 34, 35, 72]. However, during the acceleration period the suspension loses its plasticity and is converted into a stiff matrix, which is no longer placeable. The intense hydration of C_3S during the acceleration period is associated with the formation of CSH-phases and the precipitation of portlandite. C_2S starts to hydrate. C_3A and to a lesser extent C_4AF continue to hydrate. During the acceleration period the calcium and sulfate ion concentration in the pore water are decreasing due to the ettringite formation. The pore water consists of alkali hydroxides and has a pH of 13 to 14 [73].

2.4.2.4 Deceleration Period

This stage is characterized by the hardening of the cement paste or concrete. Due to a lack of sulfate ions in the pore water, ettringite is converted into monosulfate as described in Eq. [2.10]. This effect can be seen in the heat flow diagram by a slight peak at the decreasing part of the curve ("E to M shoulder" in Fig. 2-10). During the deceleration period the hydration reactions get more and more diffusion controlled. Pore volume decreases with increasing time and decreasing w/c ratio. Having completely hydrated, the cement mainly consists of CSH-gel and portlandite [72].

2.4.3 The Importance of Adequate Sulfate Concentration

2.4.3.1 Rheological Model

As previously mentioned, gypsum is added to cement clinker in order to control the setting of the cement and the hydration of C_3A. The hydration is controlled by providing SO_4^{2-} and Ca^{2+} ions into the pore water to form ettringite on the C_3A surfaces. If there is an adequate sulfate and calcium ion concentration, ettringite will be the main hydration product. If there is a lack or a surplus of SO_4^{2-} and Ca^{2+} for the existing reactivity of C_3A, other phases like monosulfate or secondary gypsum (i.e. dihydrate) will occur, which are negatively affecting the fluidity. As calcium is dissolved from various components (cement main phases, gypsum,
free lime), it is generally not the limiting component to convert C\textsubscript{3}A into ettringite. Nevertheless, there are case studies, in which rheological problems could be related to a lack of calcium ions in the pore water [44], especially when superplasticizers were used (see Chap. 2.6.4).

In the late seventies Locher [45] described a mineralogical model for the initial fluidity of cement paste based on the hydration products of C\textsubscript{3}A (Fig. 2-11). There are many publications, in which rheological problems can be explained by this model [31, 43, 74-76]. Technically produced clinker and different ratios of anhydrite and hemihydrate were ground to cement. In the case of normal setting, C\textsubscript{3}A was exclusively converted into ettringite. In the case of an insufficient supply of sulfates, monosulfate was formed. In the case of an excessive supply, secondary gypsum precipitated besides ettringite. In the presence of a large quantity of alkali sulfates, syngenite was detected. The higher the C\textsubscript{3}A reactivity, the more sulfates were needed to impart good fluidity.

In the first two columns of Fig. 2-11 normal setting is achieved, since the sulfate ion concentration in the pore water corresponds to the reactivity of C\textsubscript{3}A (case I and II). Fluidity is easily controlled by a low reactivity of C\textsubscript{3}A (case I). Higher clinker reactivity needs more calcium sulfates and leads to a higher ettringite amount. Therefore, the second combination has a shorter setting time (case II). As long as the hydrates are not large enough to bridge the space between particles, the cement paste is still workable. This is no longer possible in the case of a lack or a surplus of sulfates (case III and IV). In case III only during the very first seconds small amounts of ettringite are formed. Afterwards, the main phases are plate-like crystals of monosulfate or calcium aluminate hydrates. An excess of sulfates (case IV) yields to the precipitation of thin and long lath-shaped secondary gypsum besides ettringite. In both cases the newly formed minerals have a negative influence on the rheological properties due to their morphology. The stiff consistency resulting from monosulfate ("flash set") can not be improved. An improvement is possible in the case of newly formed secondary gypsum ("false set") by mechanical mixing or vibrating of the concrete. This is thought to be caused by breaking up the bridges between the secondary gypsum plates and the surrounding grains. In order to allow good setting, it is suggested that cement should contain an appropriate amount of fast dissolving hemihydrate and slow dissolving natural anhydrite. Natural anhydrite plays a secondary role at the beginning of the hydration, but it is important to provide a sufficient quantity of sulfates for the subsequent reactions during the dormant and the acceleration period.

However, there are controversial findings with regard to the influence of sulfates on C\textsubscript{3}A dissolution. Although the hydration products of C\textsubscript{3}A depend on the quantity of sulfates ions in the pore water, the amount of C\textsubscript{3}A dissolution did not change in the case studies of Odler and Locher [43, 72]. They concluded that the rheological changes due to the addition of
calcium sulfates were not related to an excessive $C_3A$ hydration, but only to the different hydrates formed. However, Tang found the opposite [44]. The presence of soluble sulfates retarded the initial $C_3A$ dissolution determined by XRD. Additionally, paste flow two minutes after mixing could be related to the dissolved quantity of $C_3A$. The lower the $C_3A$ dissolution was, the higher the initial paste flow.

### 2.4.3.2 Influence of Temperature

The solubility of the sulfate containing phases (i.e. calcium sulfates, alkali sulfates) changes with temperature. On the one hand the solubility of the hemihydrate significantly decreases by increasing the temperature (Fig. 2-9). On the other hand the solubility of alkali sulfates increases with temperature [77]. For this reason it is not obvious, whether the total soluble sulfate ion content decreases or increases with an increasing temperature of the cement paste.

![Mineralogical model of the early cement hydration](image)

**Fig. 2-11:** Mineralogical model of the early cement hydration. The reactivity of $C_3A$ and the availability of sulfate ions have to be adjusted to each other in order to obtain ettringite as single hydration product and thus good concrete fluidity [45].
In general, hydration reactions in cement are increased at elevated temperature [49, 74, 78, 79]. This is also valid for the initial hydration stage [80, 81] and for the dissolution of C₃A [82]. Hence, at a higher temperature more sulfate ions are needed to convert C₃A into ettringite. Scholz studied the effect of various calcium sulfates on the consistency of concrete [83]. By varying the temperature of the systems, the author related the rheological changes to a surplus or a deficit of soluble sulfate ions in order to satisfy the C₃A conversion into ettringite.

### 2.5 Superplasticizers

#### 2.5.1 Introduction

According to EN 934-2, concrete admixtures are materials that are added to the concrete during the mixing process in quantities not larger than 5 per cent by mass of cement in order to alter its properties in its fresh and hardened state. Superplasticizers are one type of concrete admixtures. In general, they can be used in two ways [Fig. 2-12]. For the same fluidity they allow to reduce the w/c ratio by up to about 30% [34]. This implies a reduced pore volume and therefore an increased compressive strength. On the other hand they can be used as fluidifying agents, which means that the fluidity is improved at constant w/c ratio.

![Fig. 2-12: Utilization of superplasticizers: a higher fluidity at constant w/c ratio leads to self-compacting concrete (a). A reduced w/c ratio makes a concrete more durable (application: high-strength concrete) (b).](image-url)
2.5.2 Today’s Products

Today, there are three commonly used types of superplasticizers: salts of sulfonated melamine formaldehyde polymers (polymelamine sulfonates; PMS), salts of sulfonated naphthalene formaldehyde polymers (polynaphthalene sulfonates; PNS), and the so-called superplasticizers of the new generation, the polycarboxylates or polymethacrylates (PC-type superplasticizers) (Fig. 2-13) [84, 85]. The last ones were found to have the best dispersion and fluidifying ability with respect to their weight.

PNS and PMS-type superplasticizers are ionic linear organic polymers with sulfonate groups at regular intervals. The sulfonic acids are neutralized by sodium or calcium counter-ions [86]. Polycarboxylates have a backbone chain consisting of acrylic or methacrylic copolymers. At the backbone chain various functional groups (polar or ionic; carboxyl, hydroxyl groups) are grafted as side chains (e.g. polyethylene oxide graft chains) [85]. The molecular mass of the superplasticizers can vary widely (e.g. from 1’400 to 88’000 g/mol in [4, 87, 88]). The highest molecular weight can be obtained with PC-type superplasticizers. This results in a larger size of the superplasticizers, which is about 30 to 150 nm according to Uchikawa [88]. Since the functional groups of the PC-type superplasticizers are weaker acids compared to sulfonate groups containing PMS and PNS-type superplasticizers, and since the ratio between mass of molecule to mass of functional groups is higher for PC molecules compared to PNS/PMS molecules, PC-type superplasticizers are weaker electrolytes. Thus, they show a lower ionic activity [85, 89]. The variations in type and length of the main and side chain of PC-type superplasticizers yields to a broad variety of new products with very variable properties [85].

Fig. 2-13: Different types of superplasticizers: repetitive molecular unit of a) Na-PMS; b) Na-PNS and c) polycarboxylate. X represents a polar (e.g. CN) or ionic (e.g. SO₃⁻) group, R₁ represents H or CH₃ and R₂ represents a polyether side chain (e.g. polyethylene oxide) [85].
2.6 Cement–Superplasticizer Interactions

2.6.1 Introduction

Superplasticizers are introduced to cementitious suspensions in order to improve the rheological properties. They can have a strong influence on the kinetics and setting characteristics of hydrating cement systems. Beyond a critical superplasticizer concentration in concrete, cement particles and aggregates sediment due to absence of yield stress [90]. The rheological properties of fresh cement paste are controlled by many factors, for instance by the dispersion characteristics between particles due to the mixing technique, type and amount of superplasticizer added, type and amount of hydration products, particle packing determined by particle size distribution etc. It is therefore difficult to discover the main factors and interactions existing between the different components in a superplasticized cement suspension.

Different superplasticizers do not produce the same fluidity with the same cement, nor does the same superplasticizer produce the same fluidity with different cements [71]. Laboratory experiments showed that the rheological properties of certain cements behave more sensitive (i.e. less robust) with respect to type and amount of added superplasticizer compared to other combinations [91]. This may be expressed by a lower fluidifying effect, rapid slump loss, over retardation, segregation, etc. In severe cases, these phenomena are called superplasticizer incompatibilities [11, 74].

According to Jolicoeur, cement-superplasticizer interactions can be divided into physical and chemical effects [70, 92]. The physical effects occur instantly (i.e. t=0) and include the superplasticizer adsorption through electrostatic and van der Waals forces, surface charging, induction of electrostatic repulsive forces and steric repulsive forces. The chemical effects are consequences of the cement hydration (i.e. t > 0). They comprise surface binding to reactive sites, alteration of early hydration reactions and hydration products.

The following chapters are dedicated to various aspects of cement-superplasticizer interactions. The impacts to the rheological properties will be discussed. The above-mentioned physical and chemical effects will be explained more in detail in Chap. 2.6.2 to Chap. 2.6.5. The last chapter (Chap. 2.6.6) highlights the literature dealing with the influence of temperature on superplasticized cement paste.
2.6.2 Superplasticizer Adsorption and Repulsion at the Cement-Solution Interface

The physical effects of superplasticizers might be studied with model suspensions \[90, 92, 93\]. It has been shown that the fluidifying effect of superplasticizers is exclusively related to the adsorbed polymers \[90\]. Thus, superplasticizers have to be adsorbed to the cement particle surface first and hereafter they ensure dispersion.

Due to the high pH in cementitious systems, the surface of cement particles is negatively charged. This is a consequence of the hydrolysis of calcium ions (see Chap. 2.4.2.1). From ESCA\(^1\) analysis it is shown that calcium ions are dissolved from the surface of the clinker without destroying the skeletal structure of the clinker minerals. This leads to a silicon (\(\text{SiO}_4^{4-}\)) or aluminum (\(\text{Al}_2\text{O}_3^{3-}\)) rich surface \[94\]. Zeta potential of cement paste was found to be positive \[95\]. Therefore, positive ions such as \(\text{Ca}^{2+}\) form a positively charged, surface-adsorbed layer around the particles \[96\]. By this means, the negatively charged hydrophilic groups of the superplasticizers (i.e. \(\text{SO}_3^-\), \(\text{COO}^-\), \(\text{OH}^-\)) adsorb on the surfaces. The adsorbed superplasticizer molecules hinder the diffusion of water and ions to the cement grain surface causing a "shielding" or "screening" effect \[96\] (Fig. 2-14a).

According to the DLVO theory\(^2\) \[97, 98\], forces acting between superplasticized cement particles comprise van der Waals forces, \(F_{\text{vdW}}\), electrostatic repulsive forces, \(F_{\text{el}}\), and steric repulsive forces, \(F_{\text{st}}\):

\[
F_{\text{tot}} = F_{\text{vdW}} + F_{\text{el}} + F_{\text{st}}
\]  \[2.14\]

Steric repulsive force is a short-range repulsive force caused by the overlapping of the adsorbed polymers. If the distance between the adsorbed polymers in Fig. 2-14b is smaller than twice the thickness of the superplasticizers, steric interaction occurs. Stability and fluidity of a cement suspension can be investigated by the zeta potential, which is in fact a mean of the electrostatic force. However, fluidity of superplastizicized cement paste does not correlate well with zeta potential, especially when PC-type superplasticizers are used (Fig. 2-15a). Nevertheless, for PNS and PMS-type superplasticizers a considerable part of the repulsive force is attributed to electrostatic repulsion \[88, 92, 99, 100\]. On the other hand cement paste flow correlates well with the interparticle force between cement particles (i.e. \(F_{\text{tot}}\)), measured with AFM\(^3\) \[88\] (Fig. 2-15b). Uchikawa calculated the influence of steric repulsive force by subtracting the electrostatic repulsive force from the interparticle force.

---

1. Electron spectroscopy for chemical analysis; determines the elements on the sample surface by irradiating the sample with soft x-ray.
2. Theory of the stability of colloidal dispersions describing the pair-wise interaction between charged particles in a dielectric medium by Derjaguin, Landau, Verwey and Overbeek.
3. Atomic force microscopy.
(F_{tot}) using a polycarboxylate-based admixture [88]. He concluded that for PC-type superplasticizers the steric repulsive force is the main repulsive force.

Fig. 2-14: In the case of electrostatic repulsion (a) particles are repelled due to the same particle charge, while in the case of steric repulsion (b) particles are repelled due to the overlapping of superplasticizer polymers [85].

Fig. 2-15: Relationship between fresh cement paste flow, interparticle force and zeta potential. Zeta potential does not correlate with cement paste flow, whereas the interparticle force measured with atomic force microscopy (AFM) does [88].
Analyses showed high-molecular polymers to be preferentially adsorbed on cement particles, while monomers and dimers remain in the pore water and do not contribute to dispersion [93, 101]. Therefore, a reduced content of low-polymerized superplasticizer molecules (i.e. monomers, dimers) should improve fluidity. Moreover, results of other studies imply an optimal polymerization degree for best fluidity properties [84, 102-104].

As charged groups of superplasticizers like SO\text{3}^-\text{, COO}^-\text{ or OH}^- interact with the particle surface by means of electrostatic forces, the chemical structure of the superplasticizer molecules is very important when regarding the superplasticizer adsorption behavior. It has been measured for a PC-type superplasticizer having carboxylic ionic groups that the adsorption increases as the charged groups per molecule increase [88]. Zeta potential increased with an increasing content of ionic groups as well. The author concluded that the magnitude of steric repulsive force is closely related to the molecular structure of the admixture [88]. This may generally be assumed for every type of superplasticizer.

2.6.3 Preferential Adsorption on Specific Surface Sites

In literature, the term "superplasticizer adsorption" is normally defined as the amount of superplasticizer, by which the pore water is depleted. After this review, a more precise termination will be used (Chap. 3.1.3.2).

It has been observed that different cements and different cement phases adsorb different quantities of superplasticizers [4]. Additionally, soluble salts like Na\textsubscript{2}SO\textsubscript{4} and the time of superplasticizer addition were found to influence the superplasticizer adsorption behavior [6, 105]. Up to a certain extent, this can be explained by the different zeta potentials of the various cement phases (Fig. 2-16). In the absence of a superplasticizer, zeta potential was found to be positive (23 mV) for C\textsubscript{3}A and negative (-9 mV) for C\textsubscript{3}S [6]. In a saturated CaSO\textsubscript{4} solution the zeta potential of C\textsubscript{3}A and C\textsubscript{3}S was shifted towards 0 and -12 mV, respectively. By this way, the addition of gypsum impedes a flash set of the cement, since the charge of the two cement phases is not oppositional anymore. If superplasticizers are added, the negatively charged superplasticizer polymers are more adsorbed on C\textsubscript{3}A, since its charge is less negative compared to the one of C\textsubscript{3}S. Therefore, negatively charged superplasticizers (especially PMS/PNS) have a higher affinity to C\textsubscript{3}A than to C\textsubscript{3}S.
Superplasticizer adsorption shows an adsorption plateau, which is called the point of surface saturation. It roughly corresponds to the amount of superplasticizer, which allows optimal fluidity [89]. By using a PNS-type superplasticizer, Nawa found the maximum adsorption value for C₃A to lie at 280 mg/g, for C₄AF at 260 mg/g, and for C₃S at 2 mg/g [6] (Fig. 2-17). The adsorbed polymer content of PC-type superplasticizers is lower [94]. For an added amount of 100 mg per 1 g C₃A, the adsorption of PNS was nearly 100%. For a PC-type superplasticizer the adsorbed amount was only about 25%. In analogy to the measurements on pure phases, superplasticizer consumption in cement pastes or mortars also depends on the phase composition of the cement. Depending on the cement, type and amount of superplasticizer used, several authors found relative adsorption values ranging from 51 to 94 wt.-% of the total amount added [3, 5]. The adsorbed amount of PNS-type superplasticizer was found to vary from 2-15 mg/g of cement, depending on the alkali content of the cement [6]. The increased adsorption was attributed to a higher content of C₃A and to higher cement fineness. The amount of adsorbed superplasticizer improves particle dispersion as discussed in Chap. 2.6.2. Thus, the influence of preferential adsorption was also seen in terms of fluidity. In order to obtain the same fluidity, more superplasticizer was needed for cements having a high content of C₃A and/or a high cement fineness [5, 11, 106, 107]. C₃A seems to have a stronger influence on fluidity compared to C₄AF [106].

Fig. 2-16: Zeta potential of C₃A and C₃S in saturated CaSO₄ solution as a function of PNS concentration [6]. In pure water the charge of C₃A and C₃S are diverse. In a saturated lime solution the addition of superplasticizer makes the C₃A particles negative due to the adsorption of the negatively charged superplasticizer polymers.
In colloid chemistry an increasing amount of electrolytes (i.e. increased ionic strength) compresses the electric double layer around particles. Therefore, the fluidity of a suspension should decrease by the fact that particles get closer together [3, 92]. For hydrating cement systems the situation is more complex, since the electrolytes are able to participate in the hydration reactions. For superplasticized cement systems it was found that the addition of soluble sulfates (K₂SO₄, Na₂SO₄, hemihydrate) reduced the adsorbed amount of PNS-type superplasticizer [3, 6, 108, 109]. This implies that sulfates hinder the adsorption on C₃A and therefore less superplasticizer polymers are incorporated into hydrates during the first minutes of cement hydration [6]. As a consequence, the addition of sulfates was found to decrease the saturation point of the adsorption isotherms [3, 6] (Fig. 2-17). Thus, by adding sulfates, less superplasticizer is needed for optimal dispersion. Because the dissolved amount and the dissolution rate of alkali sulfates is considerably higher compared to the one of calcium sulfates, the former may significantly influence the rheological properties of superplasticized cement. The amount of soluble alkali sulfates present in cement seems to be very important.

![Fig. 2-17: Adsorption isotherms for pure C₃A, C₄AF and C₃S [6]. Note the differences between C₃A/ C₄AF and C₃S adsorption. The addition of hemihydrate or Na₂SO₄ greatly decreases the amount of adsorbed PNS for C₄AF and to a lesser amount also for C₃A.](image-url)
Based on the results of many researchers [5, 71, 92, 102, 108, 110], the following simple mechanism can be concluded:

**SO$_3$ originating from PNS and sulfate ions present in the pore water compete for the same reactive sites on the hydrating cement surface, particularly on C$_3$A.**

Since PMS polymers also contain sulfonate groups at each repetitive unit, the same mechanism can be assumed. The addition of soluble sulfates increases the amount of sulfate ions in the pore water. Consequently, less superplasticizer can adsorb on the cement surfaces because a higher quantity of sulfate ions compete for the reactive sites. As the hydration of C$_3$A is very intense during the first minutes, a large amount of superplasticizer is adsorbed. An increased amount of sulfate ions in the pore water leads to a reduced superplasticizer adsorption and therefore to a reduced incorporation during the first minutes (Fig. 2-18). Thus, more superplasticizer is still available after the initial hydration period to disperse the system.

![PNS adsorption with and without soluble sulfates](image)

In terms of paste fluidity an optimal amount of soluble alkali sulfates was observed [3, 7, 109]. Jiang found this value to be around 0.4 - 0.5 wt.-% Na$_2$O-equiv of the cement weight, independent of superplasticizer amount and cement type [7]. The increase in fluidity was explained by the mechanism mentioned above. Beyond a certain level of sulfate addition, the fluidity decreased. This fact was attributed to the compression of the electric double layer due to the increased ionic strength.

Yamada discovered that the competitive behavior between PNS or PMS and sulfate ions in the pore water can also be applied to PC-type superplasticizers during the dormant period [111]. Additionally, the adsorption mechanism was found to be reversible by varying the
sulfate ion concentration in the pore water during the dormant period (Fig. 2-19). By the addition of alkali sulfates (Na$_2$SO$_4$) to the already mixed paste (i.e. during the dormant period) the fluidity decreased as predicted by the competition mechanism. Pore water revealed an increase in both the sulfate ion and superplasticizer concentration in solution (i.e. the adsorbed amount of superplasticizer decreased). This indicates that the fluidity decreased due to the reduced superplasticizer content on the cement surfaces. By subsequent addition of calcium chloride (CaCl$_2$) the fluidity increased. This was accompanied by a decrease of the sulfate ion and the superplasticizer concentration in the pore water. The decrease of sulfate ion concentration was explained by the solubility product of gypsum, which was exceeded by the addition of CaCl$_2$. As a consequence, gypsum precipitated, the sulfate ion concentration decreased, which in turn led to an increased adsorption of the superplasticizer and an improved slump flow.

Chiocchio discovered that delayed addition of PNS and PMS-type superplasticizers decreased the superplasticizer adsorption compared to direct addition. On the other hand the fluidity of the paste increased [105]. The optimum time of addition was thought to be at the start of the dormant period. At that time the initial hydration reactions have already passed and further hydration products would not adsorb large quantities of superplasticizers. Similar results were made both on pure cement phases and on cement by other researchers [94, 112]. It was therefore concluded that delayed addition reduces the adsorption on C$_3$A and enhances the adsorption on silicate phases [3, 113]. In a detailed study Uchikawa verified these findings by measuring the thickness of the hydrates formed on a polished clinker.
surface, which was dipped into an aqueous solution of PNS-type superplasticizer [4]. In the case of simultaneous superplasticizer addition the adsorbed hydrate layer thickness of C_3S and the interstitial phase (i.e. C_3A, C_4AF) was about 50 and 300 nm, respectively. At delayed PNS-type superplasticizer addition, the thickness of the adsorbed hydrates was 20 nm both for C_3S and the interstitial phase. This corresponded to the thickness of the adsorbed polymer, indicating that the molecules were not overgrown (Fig. 2-20).

For PC-type superplasticized cements both the adsorption of superplasticizer molecules and the fluidity was found to be less influenced by delayed addition [4]. This implies that PC-type superplasticizers get less incorporated in the hydration products. This may be due to a reduced hydration activity caused by the superplasticizer molecules, due to the lower ionic activity compared to PMS and PNS-type superplasticizers, or due to the larger size of PC molecules.

![Fig. 2-20: Distribution of superplasticizers at direct or delayed addition on C_3S and interstitial phase. Delayed addition of PNS-type superplasticizers greatly reduces the amount of adsorbed polymers and increases the fluidity (adapted from[4]).](image)

### 2.6.4 Complexation and Solubilization of Ionic Species

Superplasticizers were found to interfere with the solubility of the different calcium sulfates like calcium sulfate dihydrate, calcium sulfate hemihydrate or anhydrite. They may adsorb on calcium sulfates, which retards the dissolution rate and causes a flash set due to a sulfate starved system [114, 115]. Fernon showed that a Na-PNS superplasticizer improved the
solubility of dihydrate and hemihydrate, whereas natural anhydrite was only slightly affected [2]. A Ca-PNS superplasticizer only decreased the solubility of natural anhydrite. Others found PNS to be adsorbed by hemihydrate reducing its rate of solubility [70]. Other researchers state that the conversion from hemihydrate to dihydrate is retarded [2, 116]. As a consequence, the dissolved amount of calcium sulfates is increased due to an equilibrium shift.

It is thus concluded that sulfonate groups of the ionized superplasticizers are able to complex the free calcium ions present in the cement-superplasticizer solution. Calcium sulfonates are formed in the case of PMS and PNS, and chelate complexes in the case of PC-type superplasticizers [94].

It has also been reported that cement-superplasticizer irregularities may arise from an insufficient supply of dissolved calcium or aluminate ions [2, 55, 115].

### 2.6.5 Alteration of Hydration Rate and Hydration Products

Although the superplasticizer molecules are too large to get incorporated into the crystal lattice, they interact with the hydrates by intercalation (Fig. 2-21). With several investigation techniques (SEM¹, TEM², XRD, IR³) the existence of well-defined organo-mineral intercalation compounds could be proved. Sulfonate groups of a PNS-type superplasticizer were found to be chemically bound to the calcium aluminate layers [2]. Moreover, IR spectra showed preferential association between PMS and ettringite [81, 117]. Other studies showed that the initial rapid adsorption of superplasticizers seems to occur on an ettringite precursor [90, 118].

The alteration of the hydration rate depends both on the type and quantity of superplasticizer and on the cement used [102, 119]. Investigations at short hydration times (i.e. initial hydration stage and dormant period) using cement or synthesized cement phases revealed that superplasticizers could either accelerate or retard the hydration rate [69, 81, 92, 113, 117, 120-123].

Besides the forces acting between particles, the morphology of the hydrates is very relevant to the fluidity of cement or mortar pastes. It is generally believed that the use of superplasticizer alters the size of ettringite [85]. Without superplasticizer addition ettringite consists of needle-shaped, fibrous crystallite bundles of up to several 10µm in size. In the presence of superplasticizers the crystals are smaller and short-sized (< 10µm). Therefore, it is concluded that superplasticizers act as inhibitors of the crystal growth [2, 85].

---

¹. Scanning electron microscopy
². Transmission electron microscopy
³. Infra red analysis
2.6.6 Influence of Temperature

There is no extensive literature regarding the rheological behavior at different temperatures. Although it might be expected that a higher temperature leads to a lower fluidity and a higher fluidity loss (as reported in [124, 125]), this is not a general rule for all superplasticized cements.

Jolicoeur and Nawa showed that the fluidity of different cement pastes exhibits a non-linear behavior with regard to changes in mortar temperature [126, 127]. Nawa related the differences to two competitive effects:

- an increased temperature increases the amount of hydrates formed, which decreases fluidity
- an increased temperature increases the superplasticizer adsorption, which increases fluidity

However, Flatt found that the temperature dependency of superplasticizer adsorption greatly depended on the model suspensions used. A coherent influence (e.g. increased adsorption with increasing temperature) was not found [128].

Fig. 2-21: Intercalation of PNS superplasticizer molecules with calcium aluminate layers [2].
The influence of temperature on paste flow and flow loss was also found to decrease with increasing length of polyethylene oxide graft chain of the PC-type superplasticizer under study [127]. According to the author, this is attributed to steric repulsion, which is mainly governed by the length of the graft chains.

2.7 Concluding Remarks

Cement hydration is a non-linear hydration process. At different hydration times different hydration rates and different hydration reactions occur. For good fluidity and a proper setting behavior of the cement it is thus evident that the desired hydration reactions have to happen at the right time. It has been shown that the early hydration reactions are crucial for the initial flow behavior. If the sulfates are not properly adjusted to the amount of the dissolved C₃A, the rheological behavior is adversely affected due to undesired hydration products like secondary gypsum or monosulfate.

Superplasticizer molecules adsorb on the hydrating cement particles and therefore they interact with the hydration reactions. These interactions are even more pronounced at a lower w/c ratio, because the particles are closer together [129]. In relative terms, a reduced w/c ratio implies that a higher quantity of water has to be used for the hydration of C₃A and a smaller amount is available for all the other reactions (e.g. dissolution of sulfates) [54]. For cement-superplasticizer compatibility it is again the sulfate ion availability and the reactivity of C₃A, which seem to be the most important parameters for the initial flow and the fluidity loss of a given cement:

- C₃A may consume a large quantity of superplasticizer, which results in a low initial fluidity and probably in a fast fluidity loss.
- Sulfate ions compete with the negatively charged functional groups of the superplasticizers (sulfonates, carboxylates, hydroxides) for the reactive sites on the cement, particularly on C₃A.

Therefore, sulfate ion availability in the very beginning of cement hydration is a key factor. Hence, initial fluidity of cement mainly depends on cement composition (C₃A, sulfates), cement fineness, w/c ratio, superplasticizer type and amount, and temperature.
3 EXPERIMENTAL

3.1 Investigation Techniques

The following six sub-chapters describe the investigation techniques applied for mortar and cement paste (Chap. 3.1.1 to Chap. 3.1.6) as well as for the basic material cement (Chap. 3.1.7).

3.1.1 Rotational Viscometer

3.1.1.1 Cement Paste and Mortar Experiments

In this work a rotational viscometer (Viskomat PC) from Schleibinger, Germany, was used. A fixed paddle was immersed into a rotating sample container (coullette principle) and the torque applied on the paddle was measured at different rotation speeds. A paddle designed for cement paste was used for all experiments (Fig. 3-1). A cooling bath (table cryostat K 30) from Funke Medingen, Germany, enabled constant temperature conditions during the experiments. By this means, the temperature of the mortar was kept constant at ±1 °C of the desired temperature. Two measuring profiles were used (Fig. 3-2). With profile A the rheological parameters relative yield value (proportional to yield value) and relative viscosity coefficient (proportional to plastic viscosity) were determined from the downward curve measured between the 16th and the 22nd minute of the 51 minutes lasting measurement (torque vs. rotation speed-diagram). These values depend on the geometric specifications of the viscometer (Chap. 2.3.2) and will hereafter be referred to as **relative yield value** and **relative viscosity coefficient**. Relative yield value is defined as the ordinate of the linear regression, whereas the relative viscosity coefficient is defined as the slope of this line. The difference in the measured torque at 120 rpm between the 15th and the 51st minute was defined as the **stiffening value**. Positive values indicate that the torque increased during
measurement. Profile B was measured at constant rotation speed (120 rpm) for 30 minutes (Fig. 3-2). It was used to determine differences caused by the delayed addition of inorganic salts (Chap. 4.2.3.4). A two-point calibration of the rotational viscometer was made at 0.0 and 156.1 Nmm.

Fig. 3-1: Rheological testing apparatus "Viskomat PC" with the paddle designed for cement paste.

Fig. 3-2: Measuring profiles used for the experiments. Profile A was used for the evaluation of the rheological parameters, profile B (30 min at 120 rpm) for the effect of delayed addition of inorganic salts.
3. EXPERIMENTAL

3.1.1.2 Concrete Experiments

The rheological parameters relative yield value [Nm] and relative viscosity coefficient [Nm·s] were measured with a coaxial cylinders viscometer (BML WO-3) from ConTec, Iceland, using the FreshWin software for data evaluation. The viscometer is based on the Couette rheometer principle, where the inner cylinder measures the torque as the outer cylinder rotates at variable rotation velocity. The inner and outer cylinders were adjusted for concretes having grain size diameters smaller than 16mm (C-200 measuring system). The standard measuring profile was used in order to evaluate the rheological parameters (Fig. 3-3).

![Fig. 3-3: Measuring profile for concrete of the BML viscometer.](image-url)
3.1.2 Ion Chromatography (IC)

Ion chromatography measurements were performed with a Dionex DX 5000 system using a PeakNet software release 4.30 from Dionex, Switzerland. Measuring parameters for the detection of Na\(^+\), K\(^+\) and SO\(_4\)\(^{2-}\) are shown in Tab. 3-1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Anions</th>
<th>Cations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity detector</td>
<td>CD20</td>
<td></td>
</tr>
<tr>
<td>Gradient pump</td>
<td>GP40</td>
<td></td>
</tr>
<tr>
<td>Injection volume [µl]</td>
<td>100 µl</td>
<td></td>
</tr>
<tr>
<td>Injection mode</td>
<td>full loop</td>
<td></td>
</tr>
<tr>
<td>High pressure limit [psi]</td>
<td>3500</td>
<td>3500</td>
</tr>
<tr>
<td>Suppressor</td>
<td>ASRS-Ultra 4-mm</td>
<td>CSRS-Ultra 4-mm</td>
</tr>
<tr>
<td>Suppressor’s current [mA]</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Column type</td>
<td>AS 14</td>
<td>CS 12</td>
</tr>
<tr>
<td>Eluent</td>
<td>3.5 mN Na(_2)CO(_3) / 1 mN NaHCO(_3)</td>
<td>22 mN H(_2)SO(_4)</td>
</tr>
<tr>
<td>Calibration</td>
<td>4-point calibration SO(_4)(^{2-}): 0, 10, 50, 100 ppm</td>
<td>4-point calibration Na(^+): 0, 1, 2, 10 ppm K(^+): 0, 1, 2, 10 ppm</td>
</tr>
</tbody>
</table>

Tab. 3-1: Measuring parameters of the ion chromatography analyses.

3.1.3 Total Carbon Analyzer (TOC)

3.1.3.1 Instrumental Setup

In order to measure the superplasticizer concentration in the pore water, the carbon content (C\(_{org}\)) was determined. By this means, it is not possible to include different polymerization and dissociation degrees of the superplasticizers. A total carbon analyzer TOC-5000 from Shimadzu, Switzerland, was used. The method is based on the combustion of organic compounds and further detection of CO\(_2\) with non-dispersive infrared analysis. Prior to measurement, the aqueous samples were acidified with HCl 37% and sparged in order to eliminate volatile organic compounds like solvents (NPOC, non-purgeable organic content). Other measuring conditions included a three-point calibration curve (0, 50 and 100 ppm C\(_{org}\)), a baseline corrected integration of the peak area, a triple measurement of each sample, 35µl injection volume, 680\(^\circ\)C combustion temperature, and a flow rate of 150ml/min using high purity air as carrier gas.
3. EXPERIMENTAL

3.1.3.2 Definition of Superplasticizer Contents

The distribution of superplasticizer molecules can be divided into three portions (Fig. 3-4):

- **Polymers in the pore water (\(SP_{\text{sol}}\)**), which are dissolved in the pore water (i.e. \(C_{\text{org}}\))
- **Adsorbed polymers (\(SP_{\text{ads}}\))**, which are located on the hydrating cement surface
- **Incorporated polymers (\(SP_{\text{inc}}\))**, which are incorporated in the hydration products

It follows that the total superplasticizer content (\(SP_{\text{tot}}\)), which is initially added to the mixing water, is the sum of these three parts:

\[
SP_{\text{tot}} = SP_{\text{sol}} + SP_{\text{ads}} + SP_{\text{inc}} = SP_{\text{sol}} + SP_{\text{cem}} \quad [3.1]
\]

\(SP_{\text{tot}}\) can be measured prior to the addition of cement to the mixing water. It follows from Eq. [3.1] that \(SP_{\text{cem}}\) can be expressed by:

\[
SP_{\text{cem}} = SP_{\text{tot}} - SP_{\text{sol}} \quad [3.2]
\]

\(SP_{\text{cem}}\) is of practical interest, since it is not possible to determine the portion of \(SP_{\text{ads}}\) or \(SP_{\text{inc}}\) in a hydrating cement system. Thus, \(SP_{\text{cem}}\) determines the superplasticizer content, which is adsorbed to the cement phases and/or incorporated in their hydration products.

Flatt pointed out that it is only the adsorbed superplasticizer content (\(SP_{\text{ads}}\)), which contributes to dispersion [90]. With regard to surface adsorption, \(SP_{\text{ads}}\) is in equilibrium with \(SP_{\text{sol}}\). Hence, \(SP_{\text{cem}}\) is not a direct measure of dispersion or fluidity, since it contains both \(SP_{\text{ads}}\) and \(SP_{\text{inc}}\).

---

**Fig. 3-4:** Distribution of superplasticizer polymers. The adsorbed superplasticizer content (\(SP_{\text{ads}}\)) cannot be derived from the pore water data provided by the total carbon analyzer.
3.1.4 Atomic Absorption Spectrometer (AAS)

AAS measurements were performed by a SpectrAA-400 from Varian, Germany. By using hollow cathode lamps for K and Na, the absorption intensities were measured at wavelengths of 766.5 and 589.6 nm, respectively. An air-acetylene flame was used. Calibration curves for potassium and sodium were performed at 0.0, 1.0, 2.0, 3.0 and 0.0, 0.5, 1.0, 2.0 ppm, respectively. All aqueous samples were acidified prior to measurement with 0.25 ml HCl 37% in 100 ml aqueous solution.

3.1.5 Differential Scanning Calorimeter (DSC)

DSC enables to determine cement phases, which are decomposed during heating up the probe. The analyses were performed by a Mettler DSCe 822e/700 using a crucible with a laser hole. The probes were heated up from 40 to 350°C at a heat rate of 30°C/min. Subsequent evaluation was done with a Mettler STAre software. The phases ettringite (130-150°C), dihydrate (160-170°C), hemihydrate (190-210°C), monosulfate (190-220°C), and syngenite (250-310°C) were qualitatively or semi-quantitatively (i.e. integrated peak area) detected.

3.1.6 Calorimetry

A quasi-adiabatic ToniCAL device from Toni Technik, Germany, with a DCACON 4.04 software was used to measure the heat of hydration of the ongoing hydration reactions. Fully hydrated cement paste was used in the reference cell. Measuring temperature was 30°C, w/c ratio = 0.50, and the weight of the cement was 5.0 g. Superplasticizer and Na2SO4 were added to the mixing water.

3.1.7 Characterization of Cement

Phase composition was determined by X-ray diffraction analysis (XRD). The samples were measured standardless with a Bruker AXS D8 diffractometer using CuKα (λ = 1.5405 nm) radiation, an automatic divergence slit, and a graphite monochromator with a detector slit of 0.2°. The measurements were performed at an angle range varying from 5 to 75° 2-theta, at 40 kV, 40 mA, 0.2° step size and 3 seconds counting time. The diffraction patterns of cements A-K are shown in the appendix, Fig. A-1 and Fig. A-2. Quantitative phase determination was performed by Rietveld analysis using the Autoquan 2.5.0.0 software. The phases were calculated based on crystallographic data and device parameters and were iteratively adapted to the measured diffraction diagrams by refining the phase specific parameters and the phase content [130-132]. Best quantitative XRD results were obtained by
previously determining the minor cement phases (SAL-method, see Chap. 3.2.5). The crystal modification of C₃A was analyzed between 32-35° 2-theta of a sample prepared by the SAL-method. The cubic crystal modification of C₃A shows a main diffraction peak at 33.2° 2-theta, while the orthorhombic modification shows its main peak at 33.0° 2-theta.

Two external laboratories using the DSC/TGA technique and a mass balance calculation of SO₃ carried out the phase composition of the different calcium sulfates.

Loss of ignition was taken as the loss in weight between 20 and 975°C. At the same samples the chemical composition of the cements were measured by X-ray fluorescent analysis (XRF) using a SRS 303 device from Siemens, Germany.

In order to determine the acid-soluble alkalis, 0.5g of cement was added to 30ml of high purity water and acidified with 5ml HCl 37%. The suspension was heated up for 2 minutes, filtrated (Ø=2-4µm) and analyzed with AAS. In order to determine the water-soluble alkali content, 2g of cement was added to 100ml of water, shaken for 30 minutes, filtrated with a polyethylene filter (Ø=0.45µm), and analyzed with AAS.

The density of the cements was determined by an Ultrapycnometer 1000 from QuantaChrome, Germany. Specific surface of the cement was carried out by the standard Blaine permeability apparatus Cat. L 41 from Controls, Italy, according to EN 196-6.
3. EXPERIMENTAL

IC: Dionex DX 5000
TOC: Shimadzu TOC-5000

AAS: Siemens SpectrAA-400
DSC: Mettler DSCe 822e/700

Viscometer: Schleibinger Viskomat PC
Concrete rheometer: ConTec BML WO-3

Fig. 3-5: Different testing devices
3. EXPERIMENTAL

3.2 Procedures

3.2.1 Preparation of Cement Paste and Mortar

The preparation of cement paste was performed in an air-conditioned room at 21 ± 1°C and 65 ± 5% relative humidity. The materials used for the experiments were put into a refrigerator or oven in order to obtain the desired temperature below or above room temperature. Usually, superplasticizers and soluble sulfates were dissolved in the mixing water prior to the addition of cement. The water content of the liquid superplasticizers was added up to the water content.

A Tonimix RK mixer from ToniTechnik, Germany, was used to mix water, sand and cement according to EN 196-1. The liquid phase (i.e. water, superplasticizer, dissolved sulfates) and the cement were mixed for 60 seconds at low speed (30 rpm), while sand was added automatically 30 seconds after the start. For the next 30 seconds the mixing speed was high (120 rpm). Then the cement paste was poured into the cylindrical sample container of the viscometer. Exactly 3 minutes after the start of the hydration reactions (i.e. time of water addition) the viscometer measurement was started. Most tests were performed at a w/c ratio of 0.35 and a sand to cement ratio of 0.2 (mix A). Tests without superplasticizers at a w/c ratio of 0.35 (mix B) were normally made without sand in order to stay within the measuring range of the rotational viscometer. Few experiments were made at a w/c ratio of 0.48 and a sand to cement ratio of 0.20 (mix C) in order to compare the results with mix A. The mix designs for the samples used are listed in Tab. 3-2.

In the case of delayed superplasticizer addition the superplasticizer was added 60 seconds after the start of mixing. Salts (i.e. Na₂SO₄, K₂SO₄, CaCl₂), which were added at allotted intervals of time into the sample container, were introduced as solids (profile B).

<table>
<thead>
<tr>
<th>Name</th>
<th>W/C ratio</th>
<th>Sand/Cement ratio</th>
<th>Water [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A</td>
<td>0.35</td>
<td>0.20</td>
<td>192</td>
</tr>
<tr>
<td>Mix B</td>
<td>0.35</td>
<td>no sand</td>
<td>227.5</td>
</tr>
<tr>
<td>Mix C</td>
<td>0.48</td>
<td>0.20</td>
<td>264</td>
</tr>
</tbody>
</table>

Tab. 3-2: Mix designs for mortar and cement paste.
3.2.2 Preparation of Concrete

The materials needed for the experiments (i.e. concrete, tap water, sand and aggregates) were stored at the desired temperatures (10, 20, 30°C). A Zyklos mixer with a capacity of 70 litres was used to mix the materials. For 60 seconds, cement, sand and aggregates were homogenized prior to water addition. Water was added continuously during the next 30 seconds, followed by the addition of superplasticizer (30 seconds). Finally, the mixture continued rotating for another 60 seconds. Thus, the total mixing time was three minutes.

3.2.3 Preparation of Pore Water

Cement pastes or mortars were prepared as described in Chap. 3.2.1. Additionally, after a pause of 90 seconds the samples were further mixed with the Tonimix RK mixer for 60 seconds in order to simulate the shearing conditions of the rheological measurements.

A part of the suspension was then poured into a test tube and centrifuged for 4 minutes at 3000 rpm. The remaining suspension was poured into a beaker, covered with a polythene sheet and stored at room temperature, in an oven (30°C), or in a refrigerator (10°C). The cement paste was sampled at allotted time intervals during the first two hours after the contact of water with cement. After centrifugation the liquid was exhausted with a syringe, filtrated with a 0.45 µm polyethylene filter, diluted by a factor of two, and stored in polyethylene vials for subsequent analyses.

3.2.4 Stopping of Cement Hydration

Cement hydration was stopped for DSC analysis. After a hydration time of 10 minutes, about 2-3 g of cement paste was taken from the hydrating sample and poured into an agate mortar. Some millilitres of acetone were added and the suspension was ground with a pestle for 2 minutes. The suspension was then poured into a petri dish and dried with a UV lamp at 40 to 50°C. As soon as the acetone had visibly disappeared, the sample was analyzed with DSC.

3.2.5 Preparation for Powder Diffractometry (XRD)

In order to quantify the cement main phases, the cement was ground in anhydrous methanol in an agate mortar, dried, and stored in a small glass vial. Minor cement phases were qualitatively determined by removing the silicate phases (i.e. C₃S, C₂S) from the cement using the SAL-method. By this means, the diffraction patterns of C₃S and C₂S do not overlap the diffraction patterns of the minor phases. Additionally, it is possible to determine the crystal modification of C₃A. 60 g of salicylic acid, 300 ml of anhydrous methanol and 10 g of cement were stirred for 1 hour in a beaker. In order to avoid evaporation, the beaker was covered
with a polythene sheet. Filtration (Ø=2-4µm) was carried out under vacuum by subsequent addition of methanol in order to totally wash out the salicylic acid. 3g of the filtrate was blended with a small amount of methanol and ground with a pestle in an agate mortar. The finely ground suspension was dried at 30°C for about 1 hour in an oven and stored in small glass vials.

3.2.6 Measuring Accuracy

The measuring accuracy of a procedure is the sum of several measuring errors: inhomogeneous sample material, sample preparation, measuring accuracy of the apparatus. In Tab. 3-3 the estimated measuring accuracies of the different procedures are given.

The measuring accuracy of the rheological parameters were analyzed separately (Tab. 3-4). A sixfold measurement at low and high relative yield values was carried out. At a high relative yield value of 86 Nmm two values have to be regarded as different, if the difference is > 9 Nmm (significance level p < 0.05). At a low relative yield value of 7 Nmm the difference has to be > 3 Nmm. The relative viscosity coefficient of the fluid mixture has a significance value of > 0.01 Nmm, while the stiff mixture has a significance value of > 0.05 Nmm. The significance of the stiffening value is 1.2 Nmm for the mixture with the low relative yield value and 4 Nmm for mixture with the high relative yield value.

Very fluid suspensions do not show a linear Bingham fluid behavior (full lines in Fig. 3-6).

It follows that relative yield values below 5 to 10 Nmm should not be evaluated quantitatively.

![Fig. 3-6: Torque applied on the paddle of the rotational viscometer vs. shear rate. At relative yield values below 5 to 10 Nmm, the linear assumption of the Bingham fluid behavior is not valid anymore.](image-url)
### 3. EXPERIMENTAL

<table>
<thead>
<tr>
<th>Method</th>
<th>Parameter</th>
<th>Estimated accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rheology</td>
<td>rel. yield value</td>
<td>± 10 % (rel.)</td>
</tr>
<tr>
<td></td>
<td>rel. viscosity coefficient</td>
<td>0.1-0.01 Nmm*min</td>
</tr>
<tr>
<td>Ion chromatography</td>
<td>Na(^+), K(^+), SO(_4)^{2-})</td>
<td>± 10 % (rel.)</td>
</tr>
<tr>
<td>TOC analysis</td>
<td>C(_{org})</td>
<td>± 5 % (rel.)</td>
</tr>
<tr>
<td>AAS</td>
<td>Na(^+), K(^+)</td>
<td>± 5 % (rel.)</td>
</tr>
<tr>
<td>Calorimetry</td>
<td>rate of heat evolution [J/gh]</td>
<td>± 5 % (rel.)</td>
</tr>
<tr>
<td></td>
<td>total heat evolved [J/g]</td>
<td>± 1 % (rel.)</td>
</tr>
<tr>
<td>QXRD</td>
<td>C(_3)S, C(_2)S</td>
<td>± 3-4 wt.-%</td>
</tr>
<tr>
<td></td>
<td>C(_3)A, C(_4)AF</td>
<td>± 1-2 wt.-%</td>
</tr>
<tr>
<td>XRF</td>
<td>CaO, SiO(_2), Al(_2)O(_3), Fe(_2)O(_3), SO(_3), Na(_2)O, K(_2)O</td>
<td>± 1, 2.5, 10, 10, 5, 5-10 % (rel.)</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>± 0.02 g/cm(^3)</td>
</tr>
<tr>
<td>Blaine</td>
<td>air permeability</td>
<td>± 50 g/cm(^2)</td>
</tr>
</tbody>
</table>

**Tab. 3-3:** Estimated measuring accuracy of the different methods applied for this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>rel. yield value [Nmm]</th>
<th>rel. viscosity coefficient [Nmm/min]</th>
<th>Stiffening value [Nmm]</th>
<th>rel. yield value [Nmm]</th>
<th>rel. viscosity coefficient [Nmm/min]</th>
<th>Stiffening value [Nmm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>86.8</td>
<td>0.295</td>
<td>9.0</td>
<td>7.1</td>
<td>0.287</td>
<td>2.2</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>2.1</td>
<td>0.012</td>
<td>1.0</td>
<td>0.7</td>
<td>0.002</td>
<td>0.3</td>
</tr>
<tr>
<td>Significance (4 σ)</td>
<td>8.4</td>
<td>0.05</td>
<td>3.9</td>
<td>2.9</td>
<td>0.01</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Tab. 3-4:** Statistical data for the rheological measurements using the Viskomat PC. A sixfold measurement was applied for the statistical analyses.
3.3 Materials

3.3.1 Cements

The investigated Swiss cements were of type CEM I 42.5 according to EN 197-1. The chemical and mineralogical composition of cements A-E is listed in Tab. 3-5. Few experiments (see Chap. 5.1.1.1, Chap. 5.1.2.1) have been performed on five other CEM I 42.5 cements (cements F, G, H, I and K). The chemical and mineralogical composition of those cements is listed in Tab. 3-6. From a rheological point of view, the C₃A content and soluble alkalis are of importance. Soluble alkalis are expressed as equivalents of water-soluble sodium and potassium (Na₂O-eq). Due to the raw materials, potassium has a considerably higher content compared to sodium. The amount of soluble alkalis is very low for cement C, high for cement A and in between for the others. C₃A content is high for cement C and low for cement B. In the cements A-E only the cubic modification was found. Cements I, K and maybe F partially contain orthorhombic C₃A (see Fig. 3-7).

![Phase modification of the C₃A. Except for cements I, K and maybe F, only the cubic modification was present. The latter cements also contain the orthorhombic modification.](image-url)
### Tab. 3-5: Chemical and mineralogical composition of cements A-E.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cem A</th>
<th>Cem B</th>
<th>Cem C</th>
<th>Cem D</th>
<th>Cem E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3S$ [wt.-%]</td>
<td>61</td>
<td>58</td>
<td>54</td>
<td>56</td>
<td>72</td>
</tr>
<tr>
<td>$C_2S$ [wt.-%]</td>
<td>16</td>
<td>10</td>
<td>20</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>$C_3A$ [wt.-%]</td>
<td>4</td>
<td>1.5</td>
<td>12.5</td>
<td>10</td>
<td>4.5</td>
</tr>
<tr>
<td>$C_4AF$ [wt.-%]</td>
<td>15</td>
<td>26</td>
<td>8</td>
<td>2</td>
<td>13</td>
</tr>
<tr>
<td>$SO_{3\text{clinker}}$ [wt.-%]</td>
<td>1.7</td>
<td>1.0</td>
<td>0.35</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>$SO_{3\text{tot}}$ [wt.-%] (XRF)</td>
<td>3.2</td>
<td>2.7</td>
<td>2.9</td>
<td>3.0</td>
<td>2.9</td>
</tr>
<tr>
<td>$Na_2O\text{-eq}_\text{(AAS)}$</td>
<td>0.95</td>
<td>0.82</td>
<td>0.52</td>
<td>0.91</td>
<td>0.75</td>
</tr>
<tr>
<td>$Na_2O\text{-eq}_{\text{sol}}$ [wt.-%] (AAS)</td>
<td>0.92</td>
<td>0.62</td>
<td>0.22</td>
<td>0.60</td>
<td>0.63</td>
</tr>
<tr>
<td>$Na_2O\text{-eq}_{\text{sol}}/\text{tot}$ [%]</td>
<td>97</td>
<td>75</td>
<td>42</td>
<td>66</td>
<td>84</td>
</tr>
<tr>
<td>Sulfatisation degree (SD) [%]</td>
<td>139</td>
<td>93</td>
<td>52</td>
<td>92</td>
<td>104</td>
</tr>
<tr>
<td>$CaSO_4\text{-2H}_2O$ [%]</td>
<td>$1.7^a/1.8^b$</td>
<td>$1.0^a/1.4^b$</td>
<td>$2.5^a/2.1^b$</td>
<td>$2.1^a/1.6^b$</td>
<td>$2.5^a/1.8^b$</td>
</tr>
<tr>
<td>$CaSO_4\text{-0.5H}_2O$ [%]</td>
<td>$0.0^a/0.2^b$</td>
<td>$0.6^a/0.2^b$</td>
<td>$1.4^a/1.6^b$</td>
<td>$0.8^a/0.8^b$</td>
<td>$0.9^a/1.0^b$</td>
</tr>
<tr>
<td>$CaSO_4$ [%]</td>
<td>$1.3^a/1.0^b$</td>
<td>$1.4^a/1.5^b$</td>
<td>$1.0^a/1.2^b$</td>
<td>$1.1^a/1.6^b$</td>
<td>$0.4^a/0.9^b$</td>
</tr>
<tr>
<td>Density [g/cm$^3$]</td>
<td>3.14</td>
<td>3.19</td>
<td>3.09</td>
<td>3.13</td>
<td>3.11</td>
</tr>
<tr>
<td>Blaine [cm$^2$/g]</td>
<td>2750</td>
<td>3100</td>
<td>3350</td>
<td>2950</td>
<td>2850</td>
</tr>
<tr>
<td>Loss of ignition (LOI) [wt.-%]</td>
<td>2.4</td>
<td>2.9</td>
<td>3.4</td>
<td>3.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Cement phases are calculated by QXRD. Quantification of calcium sulfates was done by two external laboratories ($a$, $b$). The calculation of the sulfatisation degree (see Eq. 2.13) was done with the alkali content of the cement (*).
3.3.2 Superplasticizers

Superplasticizers based on polymelamine sulfonate (Na-PMS), polynaphthalene sulfonate (Na-PMS) and polyacrylat (PC) were used. In this work the superplasticizer concentration of pastes, mortars and concretes will always be expressed as dry content of the superplasticizer, related to the weight of cement (wt.-% of cem). The content of dry solids was determined after drying the superplasticizers at 105°C. The effective superplasticizer content was estimated by subtracting impurities (i.e. salts) and low polymerized polymers from the weight of the dried superplasticizer (data were obtained by the supplier). Superplasticizer molecules with a low degree of polymerization like monomers and dimers are not believed to contribute to dispersion. Further details are given in Tab. 3-7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cem F</th>
<th>Cem G</th>
<th>Cem H</th>
<th>Cem I</th>
<th>Cem K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S [wt.-%]</td>
<td>61</td>
<td>55</td>
<td>60</td>
<td>56</td>
<td>47</td>
</tr>
<tr>
<td>C₂S [wt.-%]</td>
<td>13</td>
<td>20</td>
<td>13</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>C₃A [wt.-%]</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>8.5</td>
<td>11.5</td>
</tr>
<tr>
<td>C₄AF [wt.-%]</td>
<td>9.5</td>
<td>11</td>
<td>13</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>SO₃ [wt.-%] (XRF)</td>
<td>2.8</td>
<td>3.0</td>
<td>2.4</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>SO₃ [wt.-%] (XRF)</td>
<td>0.88</td>
<td>1.25</td>
<td>1.10</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Na₂O-eq [wt.-%] (AAS)</td>
<td>0.95</td>
<td>0.87</td>
<td>0.86</td>
<td>0.91</td>
<td>1.03</td>
</tr>
<tr>
<td>Na₂O-eq [wt.-%] (AAS)</td>
<td>0.70</td>
<td>0.64</td>
<td>0.60</td>
<td>0.48</td>
<td>0.44</td>
</tr>
<tr>
<td>Na₂O-eq / tot [%]</td>
<td>74</td>
<td>73</td>
<td>70</td>
<td>53</td>
<td>43</td>
</tr>
<tr>
<td>Sulfatisation degree (SD) [%]</td>
<td>128</td>
<td>112</td>
<td>100</td>
<td>43</td>
<td>30</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>3.10</td>
<td>3.13</td>
<td>3.13</td>
<td>3.11</td>
<td>3.07</td>
</tr>
<tr>
<td>Blaine [cm²/g]</td>
<td>3200</td>
<td>3200</td>
<td>2500</td>
<td>2800</td>
<td>3150</td>
</tr>
<tr>
<td>Loss of ignition (LOI) [wt.-%]</td>
<td>3.4</td>
<td>2.8</td>
<td>2.8</td>
<td>3.3</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Tab. 3-6: Chemical and mineralogical composition of the cements F-K.
3. EXPERIMENTAL

3.3.3 Other Materials

The sand was a standard quartz sand from Beckum, Germany, with a maximum grain size of 0.25 mm (DIN 1164/58). Grain size distribution is shown in Fig. 3-8. Inorganic salts (Na₂SO₄, K₂SO₄, FeSO₄·7H₂O, CaCl₂) were of pure quality. Deionised water was used for the preparation of cement paste and mortar. Dilution steps for the pore water analyses were carried out with high purity water.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SP-1</th>
<th>SP-2</th>
<th>SP-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical type of superplasticizer</td>
<td>(Na-) PMS</td>
<td>(Na-) PNS</td>
<td>Polyacrylate (PC)</td>
</tr>
<tr>
<td>Average molecular weight [g/mol]</td>
<td>10'000</td>
<td>1'000-2'000</td>
<td>20'000</td>
</tr>
<tr>
<td>Effective polymer content [% of solid weight]</td>
<td>95</td>
<td>80-83</td>
<td>85-87</td>
</tr>
<tr>
<td>Content of dry solids [%]</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>SO₄²⁻ [wt.-%]</td>
<td>approx. 0.1</td>
<td>approx. 2</td>
<td>approx. 1</td>
</tr>
<tr>
<td>pH</td>
<td>approx. 9-10</td>
<td>approx. 8</td>
<td>approx. 7</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>1.2</td>
<td>1.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Tab. 3-7: Chemical composition of the superplasticizers. Data are provided by the supplier.

Fig. 3-8: Grains size distribution of two batches of the quartz sand from Beckum, Germany.
3.3.4 Comparison of Mortar and Concrete

For a diploma thesis [25] rheological studies were made with mortar and compared with concrete. The materials used for these experiments are listed in Tab. 3-8.

<table>
<thead>
<tr>
<th>Cements [%]</th>
<th>CEM I 42.5</th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃A</th>
<th>C₄AF</th>
<th>SO₃</th>
<th>Na₂O-eqsol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement L</td>
<td>73</td>
<td>4</td>
<td>3.6</td>
<td>11</td>
<td>2.89</td>
<td>2.89</td>
<td>0.77</td>
</tr>
<tr>
<td>Cement M</td>
<td>52</td>
<td>18</td>
<td>10</td>
<td>7</td>
<td>2.87</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Cement N</td>
<td>58</td>
<td>9</td>
<td>3.5</td>
<td>14</td>
<td>2.63</td>
<td>0.70</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Superplasticizer</th>
<th>SP-A: PNS-type superplasticizer</th>
<th>SP-B: PC-type superplasticizer</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Mortar mix</th>
<th>w/c=0.40</th>
<th>cement: 426.8 g</th>
<th>water: 170.72 g</th>
<th>sand (&lt;1 mm): 302.5 g</th>
<th>Viskomat PC: mortar paddle was used</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Concrete mix</th>
<th>w/c = 0.40</th>
<th>cement [kg/m³]: 400</th>
<th>water [kg/m³]: 160</th>
<th>aggregates [kg/m³]: 1817.4</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Aggregates [kg/m³]</th>
<th>0-0.2 mm</th>
<th>0.2-0.5 mm</th>
<th>0.5-1 mm</th>
<th>1-3 mm</th>
<th>3-5 mm</th>
<th>5-8 mm</th>
<th>8-16 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>156.8</td>
<td>78.2</td>
<td>48.5</td>
<td>279.9</td>
<td>227.2</td>
<td>305.3</td>
<td>721.5</td>
</tr>
</tbody>
</table>

Tab. 3-8: Materials used for the comparison of mortar and concrete [25]. Phase composition was calculated by QXRD, SO₃ was analyzed by XRF, Na₂O-eqsol by AAS.
4 RESULTS

4.1 Pore Water Analysis

Pore water analysis of cement pastes with different compositions was performed (Tab.4-1). Pore water was normally sampled after a hydration time of 10, 30, 60 and 120 minutes. During the first two hours after the contact of water with cement, the measured species (i.e. Na\(^+\), K\(^+\), SO\(_4^{2-}\), C\(_{org}\)) only changed slightly. Usually, a slight decrease of the concentrations was measured.

<table>
<thead>
<tr>
<th>Test series</th>
<th>CEM I 42.5</th>
<th>W/C ratio</th>
<th>Type of SP</th>
<th>Dosage [wt.-%]</th>
<th>Salt added</th>
<th>Dosage [wt.-%]</th>
<th>Temp. [°C]</th>
<th>Measured species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B</td>
<td>0.30</td>
<td>PMS</td>
<td>0.1 - 0.4</td>
<td></td>
<td></td>
<td>20</td>
<td>norm*</td>
</tr>
<tr>
<td>2**</td>
<td>B</td>
<td>0.30</td>
<td>PMS</td>
<td>0.1</td>
<td>Na(_2)SO(_4)</td>
<td>0.0 - 1.2</td>
<td>20</td>
<td>norm*</td>
</tr>
<tr>
<td>3</td>
<td>A, B, C</td>
<td>0.35</td>
<td>PMS</td>
<td>0.2</td>
<td></td>
<td></td>
<td>20</td>
<td>norm*</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>0.30</td>
<td>PC</td>
<td>0.0 - 0.6</td>
<td></td>
<td></td>
<td>20</td>
<td>norm*</td>
</tr>
<tr>
<td>5**</td>
<td>C</td>
<td>0.30</td>
<td>PC</td>
<td>0.2</td>
<td>Na(_2)SO(_4)</td>
<td>0.0 - 0.4</td>
<td>20</td>
<td>norm*</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>0.30</td>
<td>PMS</td>
<td>0.0 - 0.8</td>
<td></td>
<td></td>
<td>10, 20, 30</td>
<td>norm*</td>
</tr>
<tr>
<td>7</td>
<td>E</td>
<td>0.30</td>
<td>PNS</td>
<td>0.2</td>
<td></td>
<td></td>
<td>10, 20, 30</td>
<td>norm*</td>
</tr>
<tr>
<td>8</td>
<td>A-E</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10, 20, 30</td>
<td>SO(_4^{2-})</td>
</tr>
<tr>
<td>9</td>
<td>E</td>
<td>0.35</td>
<td>PMS:</td>
<td>0, 0.1, 0.4</td>
<td></td>
<td></td>
<td>20</td>
<td>norm*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PNS:</td>
<td>0, 0.1, 0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC:</td>
<td>0, 0.05, 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>A-E</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10, 20, 30</td>
<td>norm*</td>
</tr>
</tbody>
</table>

Tab. 4-1: Performed test series. Test series 1-8 were sampled at 10, 30, 60 and 120 minutes; test series 9 at 10 minutes; test series 10 at 10 and 30 minutes; norm*: normally Na\(^+\), K\(^+\), SO\(_4^{2-}\) and C\(_{org}\) were measured; **: rheological data exist.
4. RESULTS

4.1.1 Superplasticizer Concentration in Pore Water

The different tests series revealed that the amount of $\text{SP}_{\text{cem}}$ (i.e. adsorbed and incorporated amount; see Eq. (3.2)) depends both on the type and amount of superplasticizer used, and on the composition of the cement. In Fig. 4-1 $\text{SP}_{\text{cem}}$ of some cement-superplasticizer combinations is shown. For cement B a plateau is reached at around 800 ppm $C_{\text{org}}$ (=0.74 mg of dried PMS/g of cem). This means that the hydrating cement surface is saturated by superplasticizer molecules. For the two combinations with cement C no plateau is reached for the added superplasticizer concentrations. The highest value of $\text{SP}_{\text{cem}}$ at 0.8 wt.-% PMS for cement C was about 7200 ppm $C_{\text{org}}$ (=6 mg of dried PMS/g of cem). Higher superplasticizer concentrations could not be measured due to a very low, muddy residue of the filtered pore water. The measured values are in line with the values presented in literature [6]. As can be seen in Fig. 4-1, $\text{SP}_{\text{cem}}$ of the cement C-PMS combinations is independent from temperature. In relative terms, $\text{SP}_{\text{cem}}$ decreases with an increasing amount of superplasticizer added as can be seen in Fig. 4-2. The relative amount of $\text{SP}_{\text{cem}}$ of cement B decreases more rapidly compared to the two systems of cement C.

![Graph showing SP_{cem} for different cement-superplasticizer combinations.](image)

**Fig. 4-1:** Absolute amount of $\text{SP}_{\text{cem}}$ (see Eq. 3.2) for different cement-superplasticizer combinations.
In Fig. 4-3 SP sol of the cements A, B and C is shown at 0.3 wt.-% PMS superplasticizer (PMS sol). After a hydration time of 10 minutes, SP sol is lowest for cement C (< 10%) and highest for cement B (~ 50%). This relation has often been cited in literature and has been related to the C3A content of the cements [3, 5]. Thus, in Fig. 4-4 the same SP sol (i.e. PMS sol) values as in Fig. 4-3 are plotted against the C3A content. SP sol decreases with an increasing C3A content of the cement.

Fig. 4-2: SP_cem in wt.-% of the added superplasticizer (SP_tot) for different cement-superplasticizer combinations.

Fig. 4-3: PMS concentration in the pore water (SP sol) of different cements vs. time depends on the type of cement used. PMS content: 0.3 wt.-%.
4. RESULTS

In Fig. 4-5 SP\textsubscript{cem} is plotted for cement E (test series 9) against SP\textsubscript{tot}. At higher concentrations SP\textsubscript{cem} of the PC superplasticizer is much lower than for the PMS or PNS superplasticizer. Thus, for the same cement SP\textsubscript{cem} increases from PC to PMS to the PNS superplasticizer.

By increasing the amount of Na\textsubscript{2}SO\textsubscript{4} dissolved in the mixing water, SP\textsubscript{cem} decreases. This tendency is illustrated in Fig. 4-6 with the results of test series 2 and 5. For the cement B-PMS combination, the addition of 0.5 wt.-% Na\textsubscript{2}SO\textsubscript{4} leads to a decrease of about 20% of the adsorbed superplasticizer (i.e. from 60% to 40%). For the cement C-PC combination, SP\textsubscript{cem} decreases by about 10% at 0.4 wt.-% Na\textsubscript{2}SO\textsubscript{4} additions.
The influence of temperature on SP_{sol} is illustrated in Fig. 4-7. Up to 0.4 wt-% PMS added to cement C, the amount of SP_{sol} is independent of temperature. At 0.6 wt-% PMS added, the amount of SP_{sol} increased from 20 to 30°C by about 25%. About the same value (~ 20%) is obtained for cement E using 0.2 wt-% PNS by increasing the temperature from 10 to 30°C.
4.1.2 Ion Concentration in Pore Water

The content of sulfate ions in the pore water was found to increase with increasing alkali content of the cement (expressed as Na$_2$O-eq$_{sol}$, see Tab.3-5). This tendency is illustrated in Fig. 4-8 at different w/c ratios. It can be seen that the sulfate ion content linearly increases with an increasing amount of Na$_2$O-eq$_{sol}$ of the investigated cements. For the cements with the low w/c ratio, the dissolved amount of SO$_4^{2-}$ vary from 0.2-0.7 wt.-%. The corresponding sulfate ion concentration was 5-20 g/l. At a w/c ratio of 10 the dissolved amount was 1.1-2.3 wt.-% with respect to the cement weight and the corresponding sulfate ion concentration 1.1 to 2.3 g/l. Thus, the dissolved amount is 3 to 5 times higher at the w/c ratio of 10, whereas the sulfate ion concentration is 4.5 to 9 times lower than in the systems with a w/c ratio of 0.35. The content of water-soluble alkalis is less dependent on the w/c ratio. Comparing the same cements, the dissolved amounts of alkalis only decrease by less than 25% at a w/c ratio of 0.35 (test series 10) compared to a w/c ratio of 50 (Tab.3-5). For instance the amount of Na$_2$O-eq$_{sol}$ of cement E increases from 0.75 to 0.95 wt.-% by increasing the w/c ratio from 0.35 to 50.

It generally follows that with respect to a w/c ratio of 10 or even higher, the dissolved amount of sulfate ions is substantially reduced at a w/c ratio of 0.35. The dissolved amount of alkali ions is only mildly influenced. The ion concentrations, however, increase, if the w/c ratio decreases.

![Fig. 4-8: Sulfate and alkali ion concentration in the pore water at different w/c ratios. Cement pastes were made without superplasticizer. SO$_4^{2-}$ content was measured at a w/c ratio of 0.35 and 10, while the Na$_2$O-eq$_{sol}$ content was measured at a w/c ratio of 0.35 (same paste as for SO$_4^{2-}$, test series 10) and 50 (Tab.3-5).](image-url)
In test series 6, 7, 8 and 10 the temperature is varied. For the test series with superplasticizer (test series 6 and 7) a temperature increase leads to an increased content of sulfate, sodium and potassium ions. The same tendency is found without superplasticizers in test series 10 for the cements A-E (Fig. 4-9). In Fig. 4-9a the sulfate ion concentration increases from 10 to 30°C for the cements A, B, D and E. Regarding cement C, the sulfate ion concentration is lower compared to the others and remains constant over the investigated temperature range. The results for the alkali ion concentration (expressed as Na₂O-eq.) are very similar compared to those obtained for the sulfate ion concentration (Fig. 4-9b). Alkali ion concentration increases with temperature for the cements A, B, D and E. For cement C the alkali ion concentration remains constant from 10 to 30°C. On the other side the sulfate ion concentrations sampled at high w/c ratios (test series 8, w/c=10) remain constant for all cements over the measured temperature range. The values are the same as plotted in Fig. 4-8 for 20°C.

![Graphs showing sulfate and alkali ion content](image)

**Fig. 4-9:** Sulfate (a) and alkali ion (b) content of the pore water for the cements A-E. In general, the ion concentrations increase with temperature.

In literature different statements exist with regard to the influence of superplasticizer on the sulfate ion concentration in the pore water (Chap. 2.6.4). In this work the influence of added amount of superplasticizer was studied at cement E in test series 9. As can be seen in Fig. 4-10, sulfate ion concentration increases by up to 20% by increasing the amount of different types of superplasticizers.
4. RESULTS

4.2 Rheological Analysis of Cement Paste and Mortar

Analyses of the rheological parameters relative yield value, relative viscosity coefficient and stiffening value provide an insight into the flow behavior of the different cements (cement A, B, C, D, E). In this chapter the rheological influence of various factors (e.g. type and amount of superplasticizer, salt addition and temperature) will be investigated. At first, results of tests carried out with and without superplasticizers using dissolved Na$_2$SO$_4$ will be presented. After that, the influence of the w/c ratio is discussed, followed by the influence of other inorganic salts. A summary of the results will conclude the chapter.

4.2.1 Tests Without Superplasticizers

Depending on the cement composition, the different cements of the classification CEM I 42.5 exhibit a different flow behavior (Fig. 4-11). For all temperatures cement C with its high C$_3$A content (12.6 wt.-%) has the highest and cement B with the lowest C$_3$A content (1.5 wt.-%) the lowest relative yield value. Relative yield value varies from 20 to 140 Nmm. In general, the relative yield value of a system increases with temperature. This temperature dependency is most pronounced for cement C. Especially the temperature increase from 20 to 30°C almost doubles the relative yield value from 80 to 140 Nmm. Regarding the other cements, the relative yield value increases by up to 20 Nmm. In Fig. 4-12 the relative yield

![Fig. 4-10: Sulfate ion concentration in the pore water as a function of the superplasticizer dosage (SP$_{tot}$). Sulfate ion concentration increases by increasing the superplasticizer amount added to the mixing water.](image_url)
value is plotted against the Na$_2$SO$_4$ content in the mixing water. As can be seen in Fig. 4-12, the relative yield value decreases by the presence of dissolved Na$_2$SO$_4$ independent of the temperature and cement used even up to very high Na$_2$SO$_4$ concentrations (8.8 wt.-% of cement).

The relative viscosity coefficient of suspensions made without superplasticizer is independent of the Na$_2$SO$_4$ content dissolved in the mixing water (Fig. 4-13). In Fig. 4-14 the relative viscosity coefficient of the cements A-E is plotted against temperature. The coefficient ranges from 0.15 to 0.35 Nm$\cdot$min. Cements C and A show a strong temperature dependency, whereas for the other three cements the dependency is less significant.

In Fig. 4-15a the stiffening value is plotted against temperature. Except for cement A, the stiffening value increases by an increase of temperature from 10 to 30°C. Fig. 4-15b shows the stiffening value as a function of the Na$_2$SO$_4$ content. The influence of Na$_2$SO$_4$ depends on the cement used. For the cements A, B and D the stiffening value decreases. For cement C a maximum value and for cement E a minimum value is obtained.
Fig. 4-12: Relative yield value vs. Na₂SO₄ added to the mixing water. The relative yield value decreases with increasing Na₂SO₄ content in the mixing water (no superplasticizers used).

Fig. 4-13: Relative viscosity coefficient vs. Na₂SO₄ added to the mixing water (no superplasticizers used).
4.2.2 Influence of Superplasticizers on Rheological Parameters

4.2.2.1 Relative Yield Value

When regarding one single cement, the dispersive effect of the three superplasticizers is different. In Fig. 4-16 the relative yield value of cement E is plotted as a function of different superplasticizer contents. Without superplasticizer the relative yield value is about 60 Nmm. With increasing superplasticizer content the relative yield value decreases. At 0.2 wt.-% of PC superplasticizer the relative yield value is reduced to zero, whereas for the other superplasticizers a content of 0.4 wt.-% is needed to reach that value. It follows that the PC...
superplasticizer has a higher capability to reduce the relative yield value compared to PMS and PNS superplasticizers. Usually, the PMS superplasticizer has a higher capability compared to the PNS superplasticizer (see the other cements in Fig. A-3 in the appendix).

Superplasticizer saturation dosage is defined as the superplasticizer concentration, at which further addition of superplasticizer does not reduce the relative yield value significantly. Concentrations above the saturation dosage may lead to strong segregation and bleeding. In Fig. 4-16 the saturation dosage lies between 0.2 and 0.4 wt.-% PMS and PNS, since in between these two concentrations a relative yield value of zero is reached. For the PC superplasticizer the saturation dosage is less than 0.2 wt.-%, but higher than 0.1 wt.-%. In Tab.4-2 the saturation dosages of the 15 cement-superplasticizer combinations are listed. Both the capability to reduce the relative yield value and the influence of the C3A content of the different cements are clearly visible. For cement B (low C3A content) the saturation dosage is reached at a lower superplasticizer concentration compared to cement C (high C3A content). The other saturation dosages lie in between.

![Graph](Cem E, w/c=0.35)

**Fig. 4-16:** Relative yield value of cement E vs. superplasticizer content. At equal superplasticizer concentrations, the PC superplasticizer reduces the relative yield value more compared to the PMS and PNS superplasticizers.

<table>
<thead>
<tr>
<th>Superplasticizer \ Cement</th>
<th>Cem A</th>
<th>Cem B</th>
<th>Cem C</th>
<th>Cem D</th>
<th>Cem E</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMS [wt.-%]</td>
<td>0.2 - 0.4</td>
<td>0.1 - 0.2</td>
<td>0.4 - 0.8</td>
<td>0.2 - 0.4</td>
<td>0.2 - 0.4</td>
</tr>
<tr>
<td>PNS [wt.-%]</td>
<td>0.2 - 0.4</td>
<td>0.1 - 0.2</td>
<td>0.8 - 1.2</td>
<td>0.2 - 0.4</td>
<td>0.2 - 0.4</td>
</tr>
<tr>
<td>PC [wt.-%]</td>
<td>0.1 - 0.2</td>
<td>0.05 - 0.1</td>
<td>0.2 - 0.4</td>
<td>0.1 - 0.2</td>
<td>0.1 - 0.2</td>
</tr>
</tbody>
</table>

**Tab. 4-2:** Saturation dosage of the different cement-superplasticizer combinations.
In Fig. 4-17a-e the relative yield value of all 15 cement-superplasticizer combinations are plotted against temperature ("temperature characteristics"). Due to the cement composition and the efficacy of the different superplasticizers, different superplasticizer concentrations had to be used for the various cement-superplasticizer combinations. For cement C the concentration is higher and for cement B it is lower compared to the cements A, D and E, which are identical. Almost every cement-superplasticizer combination shows a peculiar temperature characteristic. Regarding for instance cement A, the combination using the PMS superplasticizer shows little variations due to changes in temperature. The combination using the PNS superplasticizer exhibits a very high relative yield value at 8°C. Finally, the combination using the PC superplasticizer shows a decreasing relative yield value with increasing temperature.

As already discussed in the literature review, alkali sulfates have a marked influence on the fluidity of superplasticized cements. At an optimal content of soluble alkali sulfates the slump or mini-slump spread was highest, whereas at lower or higher contents it was smaller (Chap. 2.6.3). In this study the relative yield value of most of the superplasticized cement combinations showed a marked influence of Na$_2$SO$_4$ added to the mixing water. This impact has been investigated on several cement-superplasticizer combinations at different temperatures.

In Fig. 4-18a,b the relative yield value of PMS, PNS and PC superplasticized cement C is plotted against the Na$_2$SO$_4$ content. For the PMS superplasticized mortar the relative yield value increases with temperature at 0.0 wt.-% Na$_2$SO$_4$. When adding Na$_2$SO$_4$ the suspensions show minimal relative yield values at 20 and 30°C at around 0.4 wt.-% Na$_2$SO$_4$. At 8°C the relative yield values increase with increasing Na$_2$SO$_4$ content. By using the PNS superplasticizer at the same concentration and temperature, the minimal relative yield value is reached at a higher Na$_2$SO$_4$ dosage (~ 0.8 wt.-%) compared to the combination using PMS. These results verify that the relative yield value may be decreased by the addition of Na$_2$SO$_4$. Moreover, the presented cement-superplasticizer combinations at 20 and 30°C verify the existence of a minimal relative yield value. However, it is also possible that no minimal relative yield value is attained, but only an increase of the latter. This is the case for the superplasticized mortar at 8°C in Fig. 4-18a. The influence of Na$_2$SO$_4$ with regard to the behavior of the relative yield value (i.e. decrease or increase) depends on temperature. Moreover, the concentrations of Na$_2$SO$_4$, at which minimal yield value is reached, depends on the type of superplasticizer used.
For two selected cement-superplasticizer combinations the influence of high Na\textsubscript{2}SO\textsubscript{4} contents was investigated. The results are illustrated in Fig. 4-19. After having passed a minimal relative yield value at 0.4 wt.-% Na\textsubscript{2}SO\textsubscript{4}, the relative yield value of the combination with cement C-0.4 wt.-% PMS rapidly increases. Above a content of 1.6 wt.-% Na\textsubscript{2}SO\textsubscript{4} the torque applied on the paddle exceeds the value of the technical specifications of the rotational viscometer. For the other combination the relative yield value increases up to an amount of 2.0 wt.-%. Similar to the experiments without superplasticizers (Fig. 4-12), the relative yield value further decreases at higher Na\textsubscript{2}SO\textsubscript{4} concentrations.
In order to obtain information about the influence of Na$_2$SO$_4$ at different temperatures for all cement-superplasticizer combinations, a single Na$_2$SO$_4$ dosage was added at 8, 20 and 30°C. It can generally be said that depending on the cement-superplasticizer combination, weak to strong influences are visible. In Fig. 4.20 the results are exemplarily shown for cement A. The relative yield values without added Na$_2$SO$_4$ (i.e. lines) are the same as previously presented in Fig. 4.17. The differences between with and without the addition of 0.4 wt.-% of Na$_2$SO$_4$ are small for the PC superplasticizer. For the combinations with PMS and PNS large differences exist at 30°C and 8°C, respectively. The results for the cements B to E are shown in the appendix, Fig. A.5.
4. RESULTS

4.2.2.2 Relative Viscosity Coefficient

The influence of temperature and Na$_2$SO$_4$ addition with regard to the relative viscosity coefficient is less complex compared to the relative yield value. In most cases, the relative viscosity coefficient remains constant or increases by an increasing amount of Na$_2$SO$_4$ added. As an example, the relative viscosity coefficient of the cement E-PMS combination is plotted against the Na$_2$SO$_4$ content in Fig. 4-21a. For this combination the relative viscosity coefficient increases at 8, 20 and 30°C with an increasing Na$_2$SO$_4$ content.

As temperature increases from 8 to 30°C, the relative viscosity coefficient decreases for all cement-superplasticizer combinations without additional Na$_2$SO$_4$ by 0.05 to 0.60 Nmm*min. As an example, the relative viscosity coefficient of cement D is plotted against temperature in Fig. 4-21b. A decrease of the relative viscosity coefficient from 0.45-0.50 to 0.30 Nmm*min is measured.

The type of superplasticizer influences the absolute value of the relative viscosity coefficient. In Fig. 4-21c the relative viscosity coefficient of cement A is plotted against different superplasticizer contents. Without superplasticizer, the coefficient is 0.27 Nmm*min. At a content of 0.4 wt.-% superplasticizer, the PC superplasticizer decreases the initial coefficient by 0.07, the PNS superplasticizer by 0.015, and the PMS superplasticizer by 0.04 Nmm*min. In general, it can be said that for the same system the relative viscosity coefficient is highest for the PMS superplasticizer, intermediate for the PNS superplasticizer, and lowest for the PC superplasticizer (see also Fig. A-4 in the appendix).
4.2.2.3 Stiffening Value

In Fig. 4-22a the stiffening values of approximately 360 experiments are illustrated in terms of cumulative percentages. About 70% of the mortars and pastes made with the PC superplasticizer have a stiffening value lower than 10%, whereas for the PMS and PNS superplasticizers this percentage is only 40 to 50%. This means that PC superplasticizers show a lower stiffening value compared to PMS and PNS superplasticizers.

The influence of temperature is shown in Fig. 4-22b, based on approximately 450 measurements. The experiments made at 30°C are horizontally shifted towards higher stiffening values. At 30°C only 30% of the experiments have a stiffening value lower than 10%, whereas at 8 and 20°C this percentage is about 60 to 70%. Therefore, the stiffening value generally increases with temperature, especially from 20 to 30°C. However, the experiments as previously reported for the tests without superplasticizers (Chap. 4.2.1, Fig. 4-15a) show that the stiffening values for a single cement might not always follow this rule. Similar results were obtained for superplasticized mortars (Fig. A-6 in the appendix).
The influence of different superplasticizer concentrations (SP$_{tot}$) is exemplarily plotted in Fig. 4-22c. Cements A-E are plotted against the PMS superplasticizer concentration. The values of the cements B, C and D increase up to a PMS concentration of 0.2 (-0.4) wt.-%. Afterwards the stiffening values decrease to values below the initial value. The values of the cements A and E decrease with increasing superplasticizer content without passing through a maximal value.

4.2.3 Special Aspects

4.2.3.1 Delayed Superplasticizer Addition

The time of superplasticizer addition has been extensively discussed in literature (e.g. [3, 94, 105, 112, 113]). Mainly cement suspensions containing PNS and PMS-type superplasticizers exhibited a marked amelioration of the fluidity, when the superplasticizers were added a few minutes after water addition (=delayed addition). This was attributed to the intense initial hydration reactions of C$_3$A (see Chap. 2.6.3). Superplasticizers of the new generation (PC-type superplasticizers) were only slightly or less affected. In this work the cement with the highest C$_3$A content (i.e. cement C) was chosen for the experiments in order to obtain clear
4. RESULTS

Differences in the rheological behavior. In Fig. 4-23 relative yield value is plotted against different cement-superplasticizer combinations. Compared to direct addition, relative yield value is significantly reduced for all superplasticizers by delayed addition. Moreover, the relative viscosity coefficient increased in all cases (Fig. A-7 in the appendix).

4.2.3.2 Superplasticizer Dosage and Addition of Na$_2$SO$_4$

It has been shown in the previous sections that the addition of Na$_2$SO$_4$ to superplasticized mortar may significantly influence the rheological properties (Chap. 4.2.2). The presented temperature characteristics in Fig. 4-20 and Fig. A-5 were measured at about the half of the superplasticizer saturation concentrations. How does a system react on Na$_2$SO$_4$ addition, if the superplasticizer dosage is considerably lower than this concentration?

In Fig. 4-24 the relative yield values of the cement E-PNS superplasticizer combinations are plotted against the Na$_2$SO$_4$ content. It is shown that at concentrations below 0.3 wt.-% PNS superplasticizer, no parabolic curve with a minimal relative yield value is obtained anymore. At the measured concentrations of 0.2 and 0.1 wt.-% PNS superplasticizer, the addition of Na$_2$SO$_4$ decreases the relative yield value. The same tendency was previously shown in Fig. 4-12 without superplasticizer addition. It follows that below a certain superplasticizer dosage, the addition of Na$_2$SO$_4$ does not lead to a strong change of the relative yield value. Relative yield value is just slightly decreasing with increasing Na$_2$SO$_4$ content.
4. RESULTS

4.2.3.3 Influence of W/C Ratio

Most of the experiments were performed at a w/c ratio of 0.35. A few tests series were made at a w/c ratio of 0.48 for the purpose of comparison. In Fig. 4-25 the relative yield value is plotted against the relative viscosity coefficient. As can be seen from this figure, a higher w/c ratio decreases both the relative yield value and the relative viscosity coefficient. Similar results are reported in literature [23]. The absolute stiffening values for the cements A-E vary at a w/c ratio of 0.48 from -0.5 to 1.0 Nmm and at a w/c ratio of 0.35 from 2.9 to 14.6 Nmm.

In Fig. 4-26 the temperature characteristics of the superplasticized cements B, C and D at different w/c ratios are shown. For the cements C and E the changes of the relative yield value are independent of the w/c ratio. The situation of cement B is different for the two w/c ratios. At a w/c ratio of 0.48 relative yield value increases with temperature, whereas at a w/c ratio of 0.35 the relative yield value shows a maximal value at 20°C. This indicates that a reduction of the w/c ratio may qualitatively change the temperature characteristics of mortars (e.g. increase/decrease with temperature).

![Fig. 4-24: Relative yield value as a function of Na2SO4. Below a certain superplasticizer concentration the relative yield value decreases like it does without superplasticizer.](image-url)
4.2.3.4 Addition of Other Inorganic Salts

The first part of this section deals with the question whether equal amounts of different sulfate salts (Na$_2$SO$_4$, K$_2$SO$_4$, and Fe$^{(II)}$SO$_4$$\cdot$7H$_2$O) have the same influence on the rheological parameters. The cement-superplasticizer combinations were chosen due to their different dependencies on Na$_2$SO$_4$ addition. For the combination cement E-0.2 wt.-% PNS the relative yield value slightly decreases by the addition of Na$_2$SO$_4$ (Fig. 4-27a). The addition of K$_2$SO$_4$ and Fe$^{(II)}$SO$_4$$\cdot$7H$_2$O increases the relative yield value. For the cement C-0.4 wt.-% PMS combination the addition of Na$_2$SO$_4$ and K$_2$SO$_4$ shows a minimal relative
yield value at around 0.27 wt.-% SO$_4^{2-}$. At higher SO$_4^{2-}$ contents the addition of Na$_2$SO$_4$ and K$_2$SO$_4$ shows a different behavior. The addition of Fe(II)SO$_4$$\cdot$7H$_2$O leads to an increase of the relative yield value as determined for the other cement-superplasticizer combination. It is thus evident from Fig. 4-27 that equal dosages of sulfate ions have a different influence on the relative yield value depending on the system (cement, superplasticizer).

![Fig. 4-27: Relative yield value vs. different sulfate salts added to the mixing water. Equal amounts of sulfate ions originating from different sulfate sources cause different rheological effects.](image)

The effect of delayed addition of inorganic salts was investigated with test profile B (see Chap. 3.2.1). Na$_2$SO$_4$$\cdot$10H$_2$O had to be used instead of Na$_2$SO$_4$, since Na$_2$SO$_4$ tended to build small clumps when added as powder directly to the mortar. In Fig. 4-28 the torque at 120 rpm is plotted against time. For all superplasticizers the addition of Na$_2$SO$_4$$\cdot$10H$_2$O and K$_2$SO$_4$ increases the torque, although Na$_2$SO$_4$$\cdot$10H$_2$O contains about 58 wt.-% of water. The addition of CaCl$_2$ leads to a decrease of the torque. These results are analogous to those presented by Yamada (see Chap. 2.6.3) using a PC-type superplasticizer. In his experiments the addition of Na$_2$SO$_4$ decreased the slump flow, whereas the addition of CaCl$_2$ increased it.
4. RESULTS

4.2.4 Comparison of Mortar and Concrete

For a diploma thesis [25] studies were made with mortar and compared with concrete. In Fig. 4-29 relative yield value of mortar and concrete is plotted as a function of the Na$_2$SO$_4$ content added to the mixing water. The relative yield value shows a minimum at 0.8 wt.-% Na$_2$SO$_4$. The relative viscosity coefficient of the mortar samples slightly increases, whereas it remains constant for the concrete samples.

In Fig. 4-30 the temperature characteristics of different cement-superplasticizer combinations are compared. The transferability of the temperature characteristics from mortar to concrete is mostly, but not always possible. The experiments made with cement L show a significant difference of the relative yield value at higher temperatures between mortar and concrete probes (Fig. 4-30a,b). Cement M shows a large temperature dependency for both superplasticizers. Nevertheless, mortar and concrete probes behave very similarly. The behavior of cement N is very similar for mortars and concrete and shows only slight temperature dependency.
Fig. 4-29: Relative yield value of mortar and concrete vs. Na$_2$SO$_4$ addition (adapted from [25]). Mortar and concrete show a minimal relative yield value at around 0.8 wt.-% Na$_2$SO$_4$. SP-A: PNS-type superplasticizer, SP-B: PC-type superplasticizer, see Chap. 3.3.4.
Fig. 4-30: Temperature characteristics of mortar and concrete (adapted from [25]). Temperature dependency of mortar and cement is very similar for the cements M and N. The differences are larger for cement L, especially at 30°C. SP-A: PNS-type superplasticizer, SP-B: PC-type superplasticizer, see Chap. 3.3.4.
4.3 Hydrates

Phase analysis of hydrating cement phases was performed with DSC. Four test series were performed in order to detect the presence of ettringite, monosulfate, secondary gypsum (i.e. dihydrate) and syngenite (Tab. 4-3). The results of test series 1 and 2 are shown in Fig. 4-32. It is shown that the ettringite peak (depicted as E) is increasing from cement A to cement D and further to cement C. The ettringite content (integrated peak area) is about 6 times larger for cement C at 20°C compared to cement A. Syngenite is present in cement A and D. An increase of the mortar temperature (from 10 to 30°C; test series 2) increases the ettringite amount in cement C by about 50% (integrated peak area).

By increasing the natural gypsum content in a clinker (test series 3), different phases are present depending on the gypsum content added to the clinker (Fig. 4-33). Without any additional gypsum, ettringite and monosulfate are present. By the addition of only 0.5 wt.-% of natural gypsum, the monosulfate peak disappears and only ettringite is present. Due to the increase of the natural gypsum content (2 and 6 wt.-%), the peaks of the calcium sulfate phases increase (i.e. dihydrate and hemihydrate).

In the rheological part of this work the system of test series 4 was found to show a minimal relative yield value at 0.4 wt.-% Na₂SO₄ (Fig. 4-18a). The DSC curves of this system are illustrated in Fig. 4-34. As can be seen from the figure, ettringite and the calcium sulfates are present in the cement paste. The system does not show qualitative differences in the detected phases up to an addition of 2.4 wt.-% Na₂SO₄.

<table>
<thead>
<tr>
<th>Test series</th>
<th>Cements</th>
<th>w/c ratio</th>
<th>Temperature [°C]</th>
<th>Other parameters (superplasticizer, Na₂SO₄, gypsum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cem A, C, D</td>
<td>0.35</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cem C</td>
<td>0.35</td>
<td>10, 20, 30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Clinker C</td>
<td>0.50</td>
<td>20</td>
<td>nat. gypsum (0-6 wt.-%)</td>
</tr>
<tr>
<td>4</td>
<td>Cem C</td>
<td>0.35</td>
<td>20</td>
<td>0.4 wt.-% PMS, 0-2.4 wt.-% Na₂SO₄</td>
</tr>
</tbody>
</table>

Tab. 4-3: Test series performed using the differential scanning calorimetry (DSC) analyzing technique.
4. RESULTS

**Fig. 4-32:** DSC curve of hydration products of the cements A, C and D at different temperatures. Hydration time=10 minutes; E=ettringite, DH=dihydrate, HH=hemihydrate, Syn=syngenite.

**Fig. 4-33:** DSC curve of clinker C with an increasing natural gypsum content. Without any added natural gypsum, monosulfate and ettringite is observed. With added natural gypsum the monosulfate peak disappears. Hydration time=10 minutes; E=ettringite, DH=dihydrate, HH=hemihydrate, M=monosulfate.
4.4 Heat of Hydration

In Fig. 4-35 the calorimetric data of the cements A-E are shown. The rate of heat evolution (dQ/dt; [J/gh]) varies considerably during the first hour of cement hydration. Cement C shows the most intense hydration reactions followed by cement E, D, A and B. For cement C the maximal rate of heat evolution is 70 J/g-h, which is reached 4 minutes after the start of cement hydration. Due to its high reactivity, cement C was chosen to investigate the influence of superplasticizers and Na$_2$SO$_4$ with respect to the initial hydration reactions. Tab.4-4 shows the investigated systems and the obtained results. The influence of Na$_2$SO$_4$ is small. The deviations in the total heat evolved [J/g] are less than 10% compared to the reference sample. Depending on the superplasticizer concentration, both the maximal rate of heat evolution and the total heat evolved increases by up to 15-20% compared to the reference sample.
4. RESULTS

<table>
<thead>
<tr>
<th>No.</th>
<th>Investigated system</th>
<th>dQ/dt(max) [J/g*h]</th>
<th>time (dQmax) [min]</th>
<th>Q(tot) [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cem C (reference)</td>
<td>69.1</td>
<td>3.25</td>
<td>21.8</td>
</tr>
<tr>
<td>2</td>
<td>Cem C, 0.4 wt.-% Na₂SO₄</td>
<td>67.5</td>
<td>3.75</td>
<td>22.7</td>
</tr>
<tr>
<td>3</td>
<td>Cem C, 0.2 wt.-% PMS (low)</td>
<td>68.8</td>
<td>3.4</td>
<td>21.7</td>
</tr>
<tr>
<td>4</td>
<td>Cem C, 0.5 wt.-% PMS (medium)</td>
<td>68.8</td>
<td>4.1</td>
<td>22.6</td>
</tr>
<tr>
<td>5</td>
<td>Cem C, 1.0 wt.-% PMS (high)</td>
<td>68.4</td>
<td>5.0</td>
<td>24.1</td>
</tr>
<tr>
<td>6</td>
<td>Cem C, 0.2 wt.-% PNS (low)</td>
<td>68.1</td>
<td>4.0</td>
<td>22.5</td>
</tr>
<tr>
<td>7</td>
<td>Cem C, 0.5 wt.-% PNS (medium)</td>
<td>64.4</td>
<td>4.75</td>
<td>22.3</td>
</tr>
<tr>
<td>8</td>
<td>Cem C, 1.0 wt.-% PNS (high)</td>
<td>72.1</td>
<td>4.9</td>
<td>24.8</td>
</tr>
<tr>
<td>9</td>
<td>Cem C, 1.0 wt.-% PNS (high), 0.4 wt.-% Na₂SO₄</td>
<td>78.7</td>
<td>4.0</td>
<td>25.6</td>
</tr>
<tr>
<td>10</td>
<td>Cem C, 0.1 wt.-% PC (low)</td>
<td>69.9</td>
<td>3.6</td>
<td>22.7</td>
</tr>
<tr>
<td>11</td>
<td>Cem C, 0.2 wt.-% PC (medium)</td>
<td>78.8</td>
<td>3.75</td>
<td>25.6</td>
</tr>
<tr>
<td>12</td>
<td>Cem C, 0.5 wt.-% PC (high)</td>
<td>79.8</td>
<td>3.75</td>
<td>26.3</td>
</tr>
<tr>
<td>13</td>
<td>Cem C, 0.5 wt.-% PC (high), 0.4 wt.-% Na₂SO₄</td>
<td>80.0</td>
<td>3.75</td>
<td>25.4</td>
</tr>
</tbody>
</table>

Tab. 4-4: Calorimetric data performed by the ToniCAL testing devise. w/c ratio was 0.50, temperature 30°C; superplasticizer and Na₂SO₄ were dissolved in the mixing water.
4.5 Summary of Results

Pore Water

- Superplasticizer adsorption on the cement surface and incorporation in the hydration products (i.e. SP\textsubscript{cem}) increases with an increasing reactivity of the cement (i.e. higher C\textsubscript{3}A content) and decreases by an increasing amount of Na\textsubscript{2}SO\textsubscript{4} in the pore water. These findings have been reported in literature. It is explained by competitive adsorption between soluble sulfates and sulfonate groups of the PNS superplasticizer molecules (see Chap. 2.6.3). Obviously, this concept is also adaptable for PMS and PC-type superplasticizers.

- Superplasticizer adsorption behavior depends on the type of superplasticizer. For the investigated cements SP\textsubscript{cem} was highest for the PNS superplasticizer and lowest for the PC superplasticizer.

- Sulfate ions in the pore water originate from calcium sulfates and soluble alkali sulfates from the clinker.

- Both sulfate and alkali ion concentration increase with temperature at a w/c ratio of 0.35.

- If the w/c ratio is reduced from 10 (50) to 0.35, the amount of dissolved sulfate ions is substantially reduced by a factor of 3 to 5, whereas the alkali ions are only mildly reduced by up to 25%.

Fig. 4-36: Maximal rate of heat evolution (dQ/dt) and the total heat evolved (Q\textsubscript{tot}) are increased by the presence of superplasticizers in the cement paste.
Hydrates

- The amount of ettringite produced during the first ten minutes depends on the cement and on the temperature of the mixture. The cement with the highest C₃A content contains the highest ettringite content. The amount of ettringite produced increases for the investigated cement C from 10 to 30°C by about 50%.

- The addition of Na₂SO₄ to a superplasticized system (cement C and 0.4 wt.-% PMS superplasticizer) does not lead to a qualitative change in the hydrates formed.

Heat of Hydration

- The maximal rate of heat evolution, which is reached after some minutes of cement hydration, depends very much on the cement and varies from 5 to 70 J/g*h for the investigated cements A, B, C, D and E.

- The addition of Na₂SO₄ does not change the heat of hydration significantly.

- The addition of superplasticizer to the mixing water may slightly increase the maximal rate of heat evolution and the total heat evolved during the first hour of cement hydration.

Rheological Parameters

- Tab.4-5 gives a summary of the rheological findings. The dependency of the relative yield value on the different parameters is very complex and may pass through a maximum or minimum when superplasticizers are used. Generally, a minimal relative yield value can be obtained by adding Na₂SO₄ to the mixing water. The Na₂SO₄ content to reach this minimal value varies depending on the cement and superplasticizer used as well as on the mortar temperature.

- The influence of superplasticizer concentration or temperature on the stiffening value or the relative viscosity coefficient is less complicated. In general, these rheological parameters change continuously in one direction.

- The rheological behavior of cement pastes, mortars and concretes is similar and allows the transfer of the results. This means that if a mortar probe of cement X needs more superplasticizer to reach a certain relative yield value or mini-slump compared to cement Y, this comparison is valid for concrete as well. However, especially the results from systems at temperatures above 20°C have to be handled with care.
### 4. RESULTS

<table>
<thead>
<tr>
<th>Varying parameters</th>
<th>Increasing SP content</th>
<th>Increasing w/c ratio</th>
<th>Increasing temperature</th>
<th>Increasing C₃A content</th>
<th>Increasing Na₂SO₄ content</th>
<th>Delayed SP-addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rheological parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rel. yield value (with SP)</td>
<td>decrease</td>
<td>decrease</td>
<td>variable</td>
<td>increase</td>
<td>variable</td>
<td>decrease</td>
</tr>
<tr>
<td>(without SP)</td>
<td>↓</td>
<td>↓</td>
<td>↓⇒↑</td>
<td>↑</td>
<td>↓⇒↑</td>
<td>↓</td>
</tr>
<tr>
<td>rel. viscosity coefficient (with SP)</td>
<td>⇒</td>
<td>PMS &gt; PNS &gt; PC</td>
<td>decrease</td>
<td>↓</td>
<td>no rule</td>
<td>increase</td>
</tr>
<tr>
<td>(without SP)</td>
<td></td>
<td>no rule</td>
<td></td>
<td></td>
<td></td>
<td>increase</td>
</tr>
<tr>
<td>Stiffening [Nmm]</td>
<td>decrease</td>
<td>decrease</td>
<td>increase</td>
<td>no rule</td>
<td>maybe decrease</td>
<td>decrease</td>
</tr>
</tbody>
</table>

**Tab. 4-5:** Summary of the rheological findings. Consequences of increasing superplasticizer content, w/c ratio, temperature, C₃A and Na₂SO₄ content, and influence of delayed superplasticizer addition on the rheological parameters.
5 DISCUSSION

5.1 Cement Composition

5.1.1 Sulfates

The amount of dissolved sulfates ions in pore water was found to depend on the w/c ratio (Fig. 4-8) and the temperature of the cementitious system (Fig. 4-9a). It slightly increased with increasing superplasticizer content for cement E (Fig. 4-10). For an entire hydration of Portland cement, a w/c ratio of about 0.23-0.40 is required [47]. However, at the beginning of cement hydration a considerable amount of cement particles (up to 12-20%) is not fully covered by water due to particle agglomeration [1]. These agglomerations entrap water, which is in turn not available for the initial hydration reactions. This effect is even more pronounced at low w/c ratios. At a w/c ratio of about 0.5-0.6 there is enough water for all reactions that happen during the initial hydration period (e.g. wetting of the particle surfaces, dissolution of cement phases with different solubility products, formation of hydration products) [54]. If the w/c ratio is decreased, competitive reactions increase since the water is becoming a limiting parameter. Additionally, sulfates are needed for instance to convert C₃A into ettringite. If the water content of a system is reduced, a lower amount of sulfate ions is present in the pore water (but its concentration is higher). This might cause problems due to the formation of ettringite. However, the effect of a lower w/c ratio might be compensated by faster dissolving sulfates as are for instance alkali sulfates.
5.1.1.1 Origin of Sulfates

Alkalis in cement clinker are either incorporated into the crystallite lattice of the cement phases (i.e. C₃A) or exist as soluble alkali sulfates [33, 58]. Water-soluble alkalis have a great influence on the rheological properties of cement mortar (Chap. 4.1.2). Fig. 5-1 shows the relationship between the SO₃ content of the clinker of the investigated cements (SO₃clinker of cement A-K) and the water-soluble alkali content of the cements (Na₂O-eqₗₛol). The water-soluble alkali content increases linearly with increasing SO₃ content of the clinker. Therefore, the SO₃ content of a clinker is the source of water-soluble alkalis. If for instance the alkali content (Na⁺, K⁺) of cement A (Na₂O-eqₗₛol=0.96 wt-% of cem) is converted into SO₃ under the assumption that the cations exist as Na₂SO₄ and K₂SO₄, about 75% of the SO₃ derives from the calculated alkali sulfate phases. The total SO₃ content in turn is not correlated with the soluble alkali content. This is due to the fact that the total SO₃ content is composed of SO₃ originating both from alkali sulfates and from gypsum, which is added to the clinker during grinding. The sulfatisation degree (see Eq. (2.13)) indicates at what percentage the alkalis are present as alkali sulfates. For the investigated cements (cement A-K) 7 of the 10 cements have a sulfatisation degree higher than 90%, which implies that the **alkalis are mainly present as soluble alkali sulfates**. For the cements C, I and K, which have lower sulfatisation degrees (30-52%), the alkalis are partially incorporated in other cement phases as well.

The ratio between soluble and total alkali content of the cement indicates at what percentage the alkali salts get dissolved (Tab.3-5 and Tab.3-6). This ratio varies from 42 to 97%. For the seven cements, in which the alkalis are usually present as soluble alkali sulfates (i.e. SD > 90%) the ratio is higher than 66%. It can thus be concluded that more than two third of the alkali sulfates get dissolved within the first 30 minutes after contact with water. In cement A the dissolved amount was almost 100%. Compared to this, the progress of hydration is small at that time (more than 90% of the total cement is still unhydrated). It follows that water-soluble alkali sulfates are located preferentially at the cement particle surface and are highly accessible to water. If they would be present within the clinker particles, they would not dissolve at that quantity.

During the clinker manufacture process, alkali sulfates crystallize very late from the liquid phase and are therefore usually located at the surfaces of other cement phases [56]. This may be caused because cracking takes place preferentially along the weaker clinker phases, which are for instance alkali sulfates. This implies that during the grinding process of the polymineralic clinker pellets, alkali sulfates get preferentially excavated. As a result of this mechanism, alkali sulfates can be dissolved in large quantities directly after the start of the cement hydration.
5.1.1.2 Quantity of $\text{SO}_4^{2-}$ Dissolved in the Pore Water

The water content has a significant influence on the dissolved amount of sulfate ions (Fig. 4-8). However, the dissolved amount of alkalis decreased only mildly by reducing the w/c ratio from 50 to 0.35 up to 25%. On the other hand the ionic concentrations increased (see Chap. 4.1.2). These results demonstrate that a low w/c ratio is limiting the dissolved amount of sulfate containing phases. In the case of a theoretically alkali-free cement, the sulfate ion content would still amount 0.5-1.0 wt.-% at a w/c ratio of 10 as can be seen in Fig. 4-8, whereas at a w/c ratio of 0.35 hardly any sulfate ions would be present. This effect can be ascribed to the sulfates originating from calcium sulfates, which are added to the cement clinker. If the w/c ratio is high, a large quantity of sulfate ions originating from the calcium sulfate phases dissolve and contribute to 0.5-1.0 wt.-% $\text{SO}_4^{2-}$. In the case of a low w/c ratio of 0.35, hardly any calcium sulfates are dissolved in the pore water. Additionally, sulfate ion concentration was found to be constant at different temperatures at a high w/c ratio of 10 (test series 8), whereas sulfate and alkali ion concentration remained constant or increased with temperature at a w/c ratio of 0.35 (Fig. 4-9). This is not obvious since the solubility of the calcium sulfates (first of all hemihydrate) decreases, whereas the solubility of alkali sulfates increases with temperature (Chap. 2.4.1.5 and Chap. 2.4.1.6). Thus, the dissolution of the calcium sulfates seems to have a minor and the dissolution of the alkali sulfates a mayor influence on the sulfate ion content in the pore water at a w/c ratio of 0.35. This is supported by the fact that the dissolved amount of the alkali ions is only mildly influenced by the water content. This means that alkali sulfates get dissolved for the most part even at low w/c ratios, as is 0.35, whereas calcium sulfates only dissolve partially. Therefore, it is

![Graph](image-url)
concluded that alkali sulfates are very important by providing sulfate ions into the pore water at a w/c ratio of 0.35.

The solubility of alkali sulfates varies from 6-120 g/l (see Tab.2-3). Since no qualitative differentiation of the alkali sulfates exists for the cements under study, it is not possible to give an estimation whether the analyzed pore waters were saturated in terms of different alkali sulfates or gypsum. In Tab.5-1 the ion concentrations of $\text{SO}_4^{2-}$ and $\text{Na}^+$ are listed. By calculating the recovery rate of the $\text{Na}_2\text{SO}_4$ added to the mixing water, the recovered amount was normally higher than 76%. Obviously, there is no chemical sink for the added $\text{Na}_2\text{SO}_4$ up to 1.2 wt.-% of the cement weight, since the dissolved ions ($\text{Na}^+$ and $\text{SO}_4^{2-}$) increase proportionally to the added quantities of $\text{Na}_2\text{SO}_4$ up to 40 g/l (test series 2 and 5). This indicates that the dissolved ions are only slightly used for the ongoing hydration reactions.

### Tab. 5-1: Recovery rate of $\text{Na}_2\text{SO}_4$ added to the mixing water. The sodium and sulfate ions mainly remain in the pore water.

<table>
<thead>
<tr>
<th>Test series</th>
<th>$\text{Na}_2\text{SO}_4$ [wt.-% of cem]</th>
<th>$\text{SO}_4^{2-}$ added [g/l]</th>
<th>$\text{SO}_4^{2-}$ detected [g/l]</th>
<th>recovery rate [%]</th>
<th>$\text{Na}^+$ added [g/l]</th>
<th>$\text{Na}^+$ detected [g/l]</th>
<th>recovery rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.22</td>
<td>4.91</td>
<td>1.51</td>
<td>31</td>
<td>2.42</td>
<td>1.85</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>11.16</td>
<td>10.17</td>
<td>91</td>
<td>5.49</td>
<td>4.99</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>4.40</td>
<td>3.78</td>
<td>86</td>
<td>2.20</td>
<td>1.80</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>8.80</td>
<td>8.04</td>
<td>91</td>
<td>4.40</td>
<td>3.99</td>
<td>91</td>
</tr>
</tbody>
</table>

5.1.1.3 Hydrates Detected by DSC

The results made in the test series 1 support the general agreement that after some minutes of cement hydration the ettringite content is correlated with the $C_3A$ content of the cement (Fig. 4-32). Moreover, for cement C it has been shown that the amount of ettringite produced increased with temperature. Other researchers made similar results [80-82]. Syngenite was detected in the cements A and D, but not in cement C. In literature the presence of syngenite is attributed to cements with a high content of alkalis [40, 60, 61] or $C_3A$ [33]. The experiments performed in this work support the presence of syngenite in high alkali cements, since the cements A and D contain syngenite at moderate to high alkali contents (0.59-0.96 wt.-% $\text{Na}_2\text{O}$-eqsol), whereas cement C does not contain syngenite and has a very low alkali content (0.22 wt.-% $\text{Na}_2\text{O}$-eqsol), but a very high $C_3A$ content (12.6 wt.-%).

According to Locher, an insufficient supply of sulfate ions provokes that the reactive phase $C_3A$ is converted into monosulfate instead of ettringite, which is negatively affecting the
fluidity of the paste [45]. Test series 3 reflects this behavior (Fig. 4-33). Without the addition of natural gypsum to clinker C, monosulfate and ettringite are present. The presence of monosulfate is thought to be the cause of rapid stiffening, which is detected one minute after the contact of cement with water. By only 0.5 wt.-% of natural gypsum added, rapid stiffening does not occur anymore. Meanwhile, the monosulfate peak has disappeared and only ettringite is present. The presence of high contents of natural gypsum is thought to decrease the fluidity as well (Chap. 2.4.3.1). The absence of monosulfate in the other cements proves that there were enough sulfate ions dissolved from the alkali sulfates to form ettringite and to prevent rapid stiffening. In general, it can be said that for some cements the addition of gypsum is not mandatory to impart a proper initial fluidity. For these cements the sulfates originating from the alkali sulfates are sufficient to convert C₃A into ettringite. However, since C₃A is only partially converted during the initial hydration reactions, the addition of an external sulfate source is still necessary for the C₃A conversion at later hydration stages.

Test series 4 was performed to find out, whether the rheological behavior of superplasticized cement pastes (i.e. minimal relative yield value as a function of the Na₂SO₄ content) can be explained by a change in the phase composition as discussed in Chap. 2.4.3.1 (i.e. influence of monosulfate, ettringite, secondary gypsum) and partially found in test series 3. The results showed that the phase composition is not altered by the addition of Na₂SO₄ (Fig. 4-34). From 0.0 to 2.4 wt.-% Na₂SO₄, ettringite and the calcium sulfate phases were present in similar quantities (estimated by the intensity of the DSC-peaks). It follows that the mineralogical composition of the investigated system is not the cause of the existence of a minimal relative yield value, which was observed for this cement-superplasticizer combination at 20°C (i.e. cement C-0.4 wt.-% PMS). Other parameters like the repulsive force of the superplasticizers are needed to explain this behavior.

5.1.2 Influence of Cement Composition on the Rheological Behavior

5.1.2.1 Cement Phase Composition and Rheological Behavior

Without Superplasticizers

In previous chapters the influence of the C₃A content on the rheological properties has already been mentioned. Several authors pointed out the importance of C₃A content and cement fineness with regard to the rheological properties of fresh cement paste and concrete. Both, high C₃A and high cement fineness made the cementitious suspensions less fluid [5, 6, 11, 106, 107]. Analyzing the rheological parameters with regard to the composition of the cements, a linear relationship between relative yield value and C₃A content exists for the
cements A-K (Fig. 5-2). As expected from literature, relative yield value tends to increase with increasing C₃A content. However, the correlation coefficient is low ($r^2=0.59$). The relative yield value for the three cements which contain about 6 wt.-% C₃A, varies from 30 to 70 Nmm, whereas all cements vary from 20 to 85 Nmm. It is thus impossible to compare the fluidity (or analogously the slump or slump flow) of two cements originating from different cement plants due to their C₃A content. However, an additionally investigated cement with 7.4 wt.-% C₃A (see cross tag in Fig. 5-2) originating from the same cement plant as cement C (12.6 wt.-% C₃A) shows that a reduction of about 5 wt.-% C₃A yields to a decrease of the relative yield value by about 35 Nmm. In relative terms this means that a reduction of the C₃A content by 40% leads to a reduction of the relative yield value by about 40%. Similar values are obtained by the correlation line in Fig. 5-2. A decrease by 5 wt.-% C₃A provokes a decrease in the relative yield value of 25 Nmm (-50% C₃A leads to -40% rel. yield value). These results confirm that the relative yield value is significantly influenced by the C₃A content.

Although it is known that the C₃A content has an influence on the initial hydration reactions and on the initial fluidity of cementitious suspensions, these influences have rarely been found in real cements [44]. Quite often this influence was studied by laboratory-made C₃A. By this means, the amount of C₃A in the investigated systems was well known and an influence of various C₃A contents was visible. In real cement, phase composition is generally calculated by the Bogue-formula according to ASTM C 150. However, in this study the phase composition of the different cements was determined by QXRD and the above-mentioned correlations were found. In Fig. 5-2 relative yield value is also plotted against $C_{3A}^{\text{Bogue}}$. Except for cement B, all cements have a C₃A content between 7 and 10.5 wt.-%. It is thus concluded that only due to the phase calculation using QXRD the mineralogical composition of different cements could be correlated with the rheological parameter relative yield value. Phase calculation according to the Bogue-formula does not provide the needed accuracy.
In order to find out more relevant influences, cement fineness (i.e. Blaine value) was taken into account. If the cement fineness is plotted against the relative yield value, no correlation exists (Fig. 5-3). The cement fineness varies from 2500 to 3500 $cm^2/g$. A little better, but still a bad correlation ($r^2=0.65$) was obtained when this parameter was considered furthermore with the content of C$_3$A (Fig. 5-4). Therefore, other parameters have a significant influence.

![Fig. 5-2: Relative yield value vs. C$_3$A content, calculated by different methods (QXRD: filled black symbols; Bogue equation: empty symbols). Regarding the Bogue equation, almost all cements have a C$_3$A content between 7 and 10 wt.-%.

![Fig. 5-3: Cement fineness vs. relative yield value (Cem A-K).]
If the sum of C2S and C3A is taken instead of the C3A content, the correlation coefficient is increased to 0.74 (Fig. 5-5). This result is amazing, since C2S is thought to react very slowly and does not contribute to the initial hydration reactions and thus to the initial relative yield value. It is possible that C2S acts as an indirect measure of another, yet unknown parameter, which has a significant influence on the relative yield value. C2S could be an indirect parameter of the reactivity of C3A. It is known that the amount and reactivity of C3A is increased, if the clinker is cooled down slowly [36]. This also favors the formation of C2S [47] due to the resorption of C3S by the liquid part (L) of the partial melt according to Eq. (5.1):

\[ L + C_3S \rightarrow C_2S + C_3A + C_4AF \]  

[5.1]

Therefore, C2S might be another indicator of the reactivity of the cement, which increases with increasing content of C3A. The addition of both cement phases might explain the amelioration of the correlation coefficient.

**Fig. 5-4:** Relative yield value vs. C3A*Blaine. The consideration of the cement fineness improves the correlation coefficient.
With Superplasticizers

In Fig. 5-6a and b the relative yield value of mortar with a concentration of 0.2 wt.-% PMS is plotted against C$_3$A and C$_3$A-Blaine, respectively. The correlation coefficients ($r^2$) are about 0.74 and 0.81, respectively. **Fig. 5-6c** shows that for superplasticized systems the consideration of the C$_2$S content has almost no influence on the correlation coefficient. Similar results are obtained for the PNS superplasticized mortars (see **Fig. A-8a-c** in the appendix). In **Fig. 5-6d** the same systems are displayed at higher superplasticizer contents (0.4 wt.-% PMS). The relative yield value is not linearly correlated with the considered parameters. Similar results are obtained for 0.1 wt.-% PC illustrated in **Fig. A-8d** in the appendix. This is caused by the fact, that 4 of 5 measuring points in **Fig. 5-6d** are located below the critical relative yield value. It has been shown in Chap. 3.2.6 that for relative yield values below 5 to 10 Nmm the Bingham assumption is not valid anymore. Moreover, it is assumed that the obtained relative yield values are not influenced by the cement composition anymore, but by the dispersive forces caused by the adsorbed superplasticizers. For the superplasticizer concentrations of 0.2 wt.-% PMS and PNS, all cement-superplasticizer combinations (except for cement B) show relative yield values above 10 Nmm. This means that it is allowed to compare the relative yield value between the different cements. Summarizing, the quality of the correlation of superplasticized mortars strongly depends on the superplasticizer dosage.
Regarding the rheological parameters relative viscosity coefficient and stiffening value, no correlation between those values and the composition of the cements is found. In the appendix, Fig. A-9, the rheological parameters and the cement parameters are plotted for the cements A-K.

5.1.2.2 Heat Evolution and Rheological Behavior

The maximal rate of heat evolution during the first minutes (i.e. peak I, see Fig. 2-10) varies much from cement to cement (Fig. 4-35). In Fig. 5-7 the C₃A content is plotted against the relative yield value and the maximal rate of heat evolution of peak I. Relative yield value and maximal rate of heat evolution tend to increase with an increasing amount of C₃A in the cement. Fig. 5-8 shows the relationship between the maximal rate of heat evolution and the relative yield value, which in fact is rather poor. However, relative yield value, C₃A content and maximal rate of heat evolution exhibit maximal values for cement C and minimal values for cement B. For cement D, containing about 10 wt.-% C₃A, the maximal rate of heat evolution...
evolution is similar to the values of cement A and E (cements A and E: 4, 4.5 wt.-% C₃A). These observations demonstrate again that the initial reactivity of cement does not only depend on the quantity of C₃A, but also on other parameters. Therefore, calorimetical data alone are not sufficient to characterize the initial fluidity of mortar.

Fig. 5-7: Relative yield value vs. maximal rate of heat evolution of the cements A-E: The maximal rate of heat evolution tends to increase with an increasing C₃A content.

Fig. 5-8: Maximal rate of heat evolution and relative yield value vs. C₃A content. Both maximal rate of heat evolution and relative yield value tend to increase with increasing C₃A content of the cements.
5.2 Cement–Superplasticizer Interactions

5.2.1 Superplasticizer Adsorption and Fluidity

It has been shown in the result section that cement-superplasticizer interactions are very manifold. The changes of the relative yield value of superplasticized mortars were found to depend on the cement-superplasticizer combination, on the amount of $\text{Na}_2\text{SO}_4$ added and on the mortar temperature. This chapter presents relationships between the data of the pore water experiments and the one of the flow behavior.

5.2.1.1 Superplasticizer Adsorption on Cement Particles

If a superplasticizer is added to the mixing water, it dissociates into its ionic compounds. After the start of cement hydration the negatively charged functional groups of the superplasticizers (i.e. $\text{COO}^-$, $\text{SO}_3^-$, $\text{OH}^-$) adsorb on the positively charged surfaces of the cement particle [96].

In this work the superplasticizer content in the pore water ($\text{SP}_{\text{sol}}$) was determined by measuring the total organic content ($C_{\text{org}}$). It was shown in Chap. 3.1.3.2 that the total superplasticizer content ($\text{SP}_{\text{tot}}$) could be divided into $\text{SP}_{\text{sol}}$, $\text{SP}_{\text{ads}}$ and $\text{SP}_{\text{inc}}$. Only $\text{SP}_{\text{ads}}$ contributes to dispersion, which in turn is in equilibrium with $\text{SP}_{\text{sol}}$. For cement paste, mortar or concrete $\text{SP}_{\text{ads}}$ is of great importance during the dormant period, since during this time the cementitious material has to be transported and placed.

As a result of these relations, there are two possibilities to increase fluidity at constant $\text{SP}_{\text{tot}}$ and constant cement reactivity:

- to increase $\text{SP}_{\text{ads}}$ (i.e. to shift the equilibrium between $\text{SP}_{\text{sol}}$ and $\text{SP}_{\text{ads}}$ towards $\text{SP}_{\text{ads}}$)
- to reduce $\text{SP}_{\text{inc}}$ (i.e. to increase the sum of $\text{SP}_{\text{ads}} + \text{SP}_{\text{sol}}$)

For hydrating cement systems both possibilities are very important due to the competitive adsorption between superplasticizer molecules and sulfate ions. In the literature review this competitive adsorption mechanism has already been discussed (Chap. 2.6.3). It was concluded that sulfate ions in the pore water compete with superplasticizers for the same reactive sites at the cement surface. Moreover, the mechanism was found to be reversible [111] and it can be described as follows (Fig. 5-9):
• If the sulfate ion concentration in the pore water is increased, more superplasticizer polymers are present in the pore water and less get adsorbed on the cement surface. Thus, the instant fluidity is lowered (i.e. slump/slump flow is lowered; rel. yield value is increased).

This competitive mechanism gives the answer on how $SP_{\text{ads}}$ is related to the sulfate ion content. Moreover, the mechanism can directly be used to explain the results of Yamada (Fig. 2-19) and those presented in Fig. 4-28. It was shown that the addition of $\text{Na}_2\text{SO}_4$ to the already mixed cement paste or mortar decreased the fluidity (i.e. increased the torque in Fig. 4-28 and decreased the relative slump flow in Fig. 2-19), whereas the addition of $\text{CaCl}_2$ increased it. Additionally, Yamada showed that both the sulfate ion and the superplasticizer content in the pore water are increased by the addition of $\text{Na}_2\text{SO}_4$, whereas the reverse effect was found by the addition of $\text{CaCl}_2$. $\text{CaCl}_2$ was thought to decrease the sulfate ion concentration due to the precipitation of gypsum. This behavior is exactly reflecting the competitive superplasticizer adsorption mechanism as shown in Fig. 5-9.

In order to transport and place concrete, the fluidity during the dormant period is of great importance. Since the dispersion of a cement suspension depends on $SP_{\text{ads}}$, the sulfate ion content during the dormant period partly defines the fluidity of the cement suspension as well. If the sulfate content is increased during the dormant period, less superplasticizer adsorbs on the particle surfaces as a result of the competitive adsorption mechanism. It follows that during the dormant period, best fluidity is obtained at a low sulfate ion content.
5.2.1.2 Influence of Initial Cement Hydration on Superplasticizer Adsorption

Immediately after the contact with water, the hydration of cement starts. The initial hydration reactions are very important for the superplasticizer adsorption behavior and for the rheological behavior of cement suspensions. On the one hand, superplasticizers were found to alter the mineralogical composition and morphology of the hydrates formed (Chap. 2.6.5). Especially the reduction in size of ettringite crystals from elongated needles to stubby-shaped particles may increase the fluidity of a mortar paste due to the reduced physical obstruction between the cement particles. On the other hand, fluidity of a mortar is governed by the repulsive forces induced by the adsorbed superplasticizers. For PC-type superplasticizers, these repulsive forces were found to be stronger compared to PMS and PNS-type superplasticizers due to the presence of steric repulsive forces. They are induced by overlapping of side chains of the superplasticizers (Chap. 2.6.2). With regard to the superplasticizers under study, this effect might explain the improved fluidity (i.e. reduction of relative yield value) of the PC superplasticizer compared to the other superplasticizers.

$SP_{cem}$ (i.e. $SP_{ads} + SP_{inc}$) was found to depend on the type and quantity of superplasticizer added. For the investigated system (cement E, $w/c=0.35$, $20^\circ$C), $SP_{cem}$ was found to be lowest for the PC superplasticizer, followed by the PMS and then by the PNS superplasticizer (Fig. 4-5). These differences may be explained by the polymerization degree (i.e. average molecular weight) and by the effective polymer content (Tab.3-7). It is known from literature [4, 133] that $SP_{cem}$ of PC-type superplasticizers is small. In general, PC-type superplasticizers have a larger molecule size compared to PMS and PNS-type superplasticizers. The larger size is supposed to reduce the incorporation of such superplasticizers. Additionally, it is possible that the adsorption is less strong, since PC-type superplasticizers are weaker electrolytes. Therefore, the electrostatic interactions are less intense.

Although PMS and PNS-type superplasticizers are chemically different, they are characterized by one sulfonate group at each repetitive unit. These functional units are assumed to adsorb on the cement surface and thus the adsorption mechanism is thought to be the same. Due to the different molecular weights of the investigated superplasticizers, the PNS superplasticizer (lower molecular weight) is assumed to get easier incorporated in the hydration products compared to the larger PMS superplasticizer. Additionally, the effective superplasticizer content of the PMS superplasticizer is larger than the PNS superplasticizer. This should also improve the dispersive force of the PMS superplasticizer compared to the PNS superplasticizer.

For the same amount of dried superplasticizer content, the efficacy to reduce the relative yield value was found to be most pronounced for the PC superplasticizer, followed by the
PMS and PNS superplasticizer (see Fig. A-3 in the appendix). When combining these results with the per cental $SP_{cem}$ values in Fig. 4-5, the efficiency to reduce the relative yield value is correlated with $SP_{cem}$. However, as will be shown in the following chapter, this statement cannot be generalized.

Pore water analysis showed that $SP_{cem}$ greatly depends on the phase composition of cement (Chap. 4.1.1). The more $C_3A$ a cement contains, the higher $SP_{cem}$ is. This effect is well known [5, 6, 11, 106, 107] and can be explained by the presence of a larger number of active sites at the cement surface and thus a larger amount of superplasticizer molecules is incorporated in the hydration products [2]. This incorporation implicates that less superplasticizer molecules are available during the dormant period to be adsorbed on the cement particles and to contribute to dispersion of the suspension, since the sum of $(SP_{sol} + SP_{ads})$ is reduced. This statement gives the answer on how the sum of $(SP_{sol} + SP_{ads})$ is related to the sulfate ion content.

5.2.1.3 Influence of Sulfate Ion Concentration on Relative Yield Value

Experiments carried out in this work and further results from literature [3, 108, 109, 134] showed that the addition of sulfate ions to the mixing water (added as soluble alkali sulfates) increases $SP_{sol}$ and thus reduces $SP_{cem}$ (Fig. 4-6). If no $Na_2SO_4$ is added, $SP_{cem}$ can be very high (up to 95 wt.-%). This behavior can be explained by the competitive adsorption mechanism between sulfates and superplasticizers as discussed in Chap. 5.2.1.1.

With regard to fluidity, an increased content of $(SP_{ads} + SP_{sol})$ does not necessarily lead to an increased fluidity. It was shown in this and in published work that dissolved sulfates led to a maximal fluidity at an appointed content of water-soluble sulfates (i.e. minimal relative yield value or maximal slump flow; see Fig. 5-10). The amount of soluble sulfates to reach the maximal fluidity was found to depend on the cement-superplasticizer combination and on the temperature.

By adding sulfate ions (in the from of $Na_2SO_4$) into the mixing water, Nawa generated such a behavior [134]. His results indicate that $SP_{cem}$ decreases with an increasing sulfate ion content, even if the point of maximal fluidity is exceeded (Fig. 5-11a). Similar results are obtained in this work. Pore water experiments (test series 2 and 5) confirmed that $SP_{cem}$ decreases with increasing content of dissolved sulfate ions (Fig. 5-11b). On the other hand relative yield value of cement C was reduced, whereas the one of cement B was increased. It is assumed that the experiments using cement C show the situation at the downward part of the parabolic curve (i.e. to the left of the minimal relative yield value of Fig. 5-10), whereas for cement B the upward part of the curve (i.e. to the right of the minimal relative yield value) is shown.
Fig. 5-10: Relative yield value vs. Na$_2$SO$_4$ addition. By the addition of Na$_2$SO$_4$ to the mixing water the relative yield value can be described as a parabolic curve having a minimal relative yield value.

Fig. 5-11: Pore water data combined with rheological data. SP$_{cem}$ decreases with increasing Na$_2$SO$_4$ added to the mixing water. a) maximal mortar flow at 0.8-1.2 wt.-% Na$_2$SO$_4$ [134]. b) decreasing relative yield value for cement C, increasing relative yield value for cement B (data of this work).
5.2.2 Rheological Model Based on Superplasticizer Adsorption Behavior and Sulfate Ion Content

In the last two chapters two apparently conflicting statements were found to describe maximal fluidity:

• During the dormant period a small amount of sulfate ions is favored, since this increases \( SP_{ads} \). It was shown in Chap. 5.2.1.1 that this is one possibility to increase the fluidity (i.e. to decrease the relative yield value).

• During the initial hydration period it is advantageous to have a large quantity of sulfate ions in the pore water. Sulfate ions reduce the amount of \( SP_{inc} \) and thus they increase the sum of \( SP_{ads} \) and \( SP_{sol} \). It was shown in Chap. 5.2.1.1 that this is the second possibility to increase the fluidity (i.e. to decrease the relative yield value).

It is obvious that, depending on the hydration time (i.e. initial hydration period or dormant period), different sulfate ion contents (i.e. small or large) favor an increase of fluidity. Based on these statements it is concluded that for best fluidity the sulfate ion content should be high during the initial hydration period (i.e. low \( SP_{inc} \)) and low during the dormant period (i.e. high \( SP_{ads} \)).

In Fig. 5-12 the distribution of \( SP_{sol} \), \( SP_{inc} \), \( SP_{ads} \), \( SP_{cem} \) and the estimated relative yield value during the dormant period is illustrated as a function of the sulfate ion concentration. The main relations are commented in Tab. 5-2. The mathematical relations have already been given in Eq. (3.1) and Eq. (3.2). The following findings and assumption were used for this model:

• At very low sulfate ion content, \( SP_{inc} \) is assumed to be \( SP_{tot} \). The entire amount of superplasticizer is incorporated in the hydrates.

• By increasing the sulfate ion content, \( SP_{inc} \) and \( SP_{cem} \) are reduced due to the competitive superplasticizer adsorption mechanism.

• By increasing the sulfate ion content, \( SP_{sol} \) is increased at the expense of \( SP_{cem} \).

• At very high sulfate ion contents, \( SP_{sol} \) is assumed to be \( SP_{tot} \). Due to the very high sulfate ion concentration, \( SP_{inc} \) does not exist anymore. Nevertheless, \( SP_{ads} \) is assumed to be zero due to the competitive superplasticizer adsorption mechanism (i.e. the equilibrium between \( SP_{ads} \) and \( SP_{sol} \) is strongly shifted towards \( SP_{sol} \)).

With regard to fluidity, best fluidity (i.e. relative yield value) is obtained at the maximal amount of \( SP_{ads} \). Assuming a cement-superplasticizer system to be situated to the left of this maximum (position \( A \) in Fig. 5-12), an increase of the sulfate ion concentration would increase both \( SP_{ads} \) and fluidity. This increase has been performed by the rheological
experiments by means of \( \text{Na}_2\text{SO}_4 \) addition to the mixing water (Chap. 4.2.2.1) and discussed in Chap. 5.2.1.3. Since the addition of \( \text{Na}_2\text{SO}_4 \) decreased the relative yield value (i.e. increased fluidity), such systems are called underdosed in terms of \( \text{Na}_2\text{SO}_4 \) addition. Assuming a cement-superplasticizer system to be situated at the maximum (position B) or to the right of this maximum (position C), the addition of sulfate ions will always lead to a lower \( \text{SP}_{\text{ads}} \) and therefore to a higher relative yield value (i.e. a lower fluidity). Hence, such systems are called overdosed in terms of \( \text{Na}_2\text{SO}_4 \) addition.

**Fig. 5-12:** Distribution of superplasticizers as a function of sulfate ion concentration in the dormant period. \( \text{SP}_{\text{ads}} \) is derived by subtracting \( \text{SP}_{\text{inc}} \) from \( \text{SP}_{\text{cem}} \). Minimal relative yield value is reached at maximal \( \text{SP}_{\text{ads}} \) (position B). The figure is divided into a low (I), intermediate (II) and a high (III) sulfate sector (see Tab. 5-2).

### Tab. 5-2: The effect of a high and a low sulfate ion concentration on fluidity and rel. yield value.

<table>
<thead>
<tr>
<th>( \text{SO}_4^{2-} ) addition to mixing water</th>
<th>initial hydration period</th>
<th>dormant period</th>
<th>fluidity ((t=10-15\text{min}))</th>
<th>rel. yield value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I</strong> low sulfate ion content</td>
<td>( \text{SP}_{\text{inc}} ) is large due to competitive SP adsorption mechanism</td>
<td>( \text{SP}<em>{\text{sol}} ) (\Leftrightarrow) ( \text{SP}</em>{\text{ads}} )</td>
<td>fluidity is low due to large amount of ( \text{SP}<em>{\text{inc}} ) (i.e. amount of ( \text{SP}</em>{\text{ads}} + \text{SP}_{\text{sol}} ) is very small)</td>
<td>high</td>
</tr>
<tr>
<td><strong>II</strong> intermediate sulfate ion content</td>
<td>( \text{SP}_{\text{inc}} ) is relatively small due to the presence of sulfate ions</td>
<td>( \text{SP}<em>{\text{sol}} ) (\Leftrightarrow) ( \text{SP}</em>{\text{ads}} ) due to the presence of sulfate ions</td>
<td>fluidity is high due to relatively large ( \text{SP}<em>{\text{ads}} + \text{SP}</em>{\text{sol}} ) and ( \text{SP}<em>{\text{sol}} ) (\Leftrightarrow) ( \text{SP}</em>{\text{ads}} ) towards ( \text{SP}_{\text{ads}} )</td>
<td>low</td>
</tr>
<tr>
<td><strong>III</strong> high sulfate ion content</td>
<td>( \text{SP}_{\text{inc}} ) is small due to competitive SP adsorption mechanism</td>
<td>( \text{SP}<em>{\text{sol}} ) (\Leftrightarrow) ( \text{SP}</em>{\text{ads}} ) towards ( \text{SP}_{\text{sol}} )</td>
<td>fluidity is low due to ( \text{SP}<em>{\text{sol}} ) (\Leftrightarrow) ( \text{SP}</em>{\text{ads}} ) towards ( \text{SP}_{\text{sol}} )</td>
<td>high</td>
</tr>
</tbody>
</table>
5.2.3 Relative Yield Value at Different Temperatures

5.2.3.1 Cements A, C, D, and E

In Chap. 4 it was shown that:

- the influence of temperature on the relative yield value depends on the cement-superplasticizer combination
- for each temperature an optimal Na$_2$SO$_4$ content exists (Fig. 4-18)

Two cement-superplasticizer combinations (Cem C-0.2 wt.% PC and Cem E-0.2 wt.% PNS) have been examined in this respect (Fig. 5-13). The Na$_2$SO$_4$-optimized systems ("opt." in Fig. 5-13) show essentially lower temperature dependencies. For the mortars with cement C, relative yield value could be reduced at 20 and 30°C by 30 to 40 Nmm, but not at 8°C. On the contrary, relative yield value of the mortar with cement E could be reduced at 8 and 20°C by 7 to 35 Nmm, but not at 30°C. It is thus possible to smooth the strong temperature dependencies of some superplasticized mortars by means of Na$_2$SO$_4$ addition.

![Fig. 5-13: Relative yield value vs. temperature with (dotted lines) and without (full lines) Na$_2$SO$_4$ added. The Na$_2$SO$_4$-optimized points ("opt." within the dotted lines) contain different amounts of Na$_2$SO$_4".](image-url)

In Fig. 5-13 the system with cement C is optimized in terms of Na$_2$SO$_4$ at 8°C. This means that at this temperature the addition of Na$_2$SO$_4$ does not provoke a change of the relative yield value. At higher temperatures the addition of Na$_2$SO$_4$ yields to a large decrease of the relative yield value. Therefore, at 20 and 30°C the system is underdosed in terms of Na$_2$SO$_4$. Contrary to this, cement E is optimized at 30°C. At lower temperatures the relative yield value is reduced by the addition of Na$_2$SO$_4$. Therefore, this system is underdosed in terms of Na$_2$SO$_4$ at 8 and 20°C.
In Fig. 5-14a-d the differences in relative yield value with and without Na₂SO₄ addition are shown as ∆yield values. A positive value means that the addition of Na₂SO₄ increases the relative yield value (i.e. the system is overdosed), whereas a negative value decreases it (i.e. the system is underdosed). These states will further be referred to as the overdosed state and the underdosed state. Regarding for instance the situation of the PNS superplasticized cement C (Fig. 5-14b), the addition of 0.4 wt.-% Na₂SO₄ increases the relative yield value by about 50 and 15 Nmm at 8 and 20°C, respectively, whereas at 30°C the relative yield value is reduced by almost 50 Nmm. For the PMS and PC superplasticizers no influence is found at 8°C. At 20 and 30°C the relative yield value is decreased by 20 to 33 Nmm. Analogous explanations can be made for the cements A, D, and E.

As indicated by the arrows in Fig. 5-14a-d, it appears that temperature has a uniform influence on the ∆yield values of a single cement. For cement C the downward arrow means that with increasing temperature the system is shifting towards the underdosed state. For the cements A, D and E the upward arrows mean that with increasing temperature the systems are shifting towards the overdosed state. Obviously, the direction of the shift (i.e. towards the underdosed or overdosed state) is exclusively related to the composition of the investigated cement. It is more or less independent on the superplasticizer used. However, the absolute ∆yield value at a given temperature still depends on the superplasticizer used. It is thus possible that at a given temperature the relative yield value can be reduced by Na₂SO₄ addition for the PNS superplasticized mortar, whereas for the PMS superplasticized mortar the relative yield value increases (see Fig. 5-14a, cement A, 8°C). The influence of the superplasticizer can be understood, since superplasticizer adsorption depends on the chemical composition of the superplasticizer (e.g. polymerization degree, length of backbone chains, kind and quantity of functional groups per molecule) as well.

For 11 out of 12 investigated cement-superplasticizer combinations the addition of 0.4 wt.-% Na₂SO₄ led to a significant change of the relative yield value (i.e. decrease or increase) at least at one of the three temperatures measured. In all cases except for one (i.e. cement C-PNS) the lowest relative yield value coincided with the temperature, at which the addition of 0.4 wt.-% Na₂SO₄ exhibited the lowest influence (see Fig. 4-20 and Fig. A-5 in the appendix). This signifies that at this temperature the investigated system was very near to its optimized state.

Hence, the temperature characteristics without Na₂SO₄ addition for the cements A, C, D and E in Fig. 4-20 and Fig. A-5 can be interpreted as follows:

- A given cement-superplasticizer combination reaches a minimal relative yield value at that temperature, where an addition of Na₂SO₄ shows the lowest influence (i.e. ∆yield value ~ 0).
For the cements A, C, D and E a schematic illustration of these findings combined with the relative yield values obtained in Fig. 4-17 is given in Fig. 5-15. The illustration is based on the following findings: a) relative yield value is minimal at the Na$_2$SO$_4$-optimized state and b) with increasing temperature the cement-superplasticizer systems with cement C are shifted towards the underdosed state, whereas the systems with cements A, D, and E are shifted towards the overdosed state.

**Fig. 5-14:** Δyield values by adding Na$_2$SO$_4$ to the mixing water vs. temperature of the superplasticized cements A, C, D and E. Negative Δyield values indicate a decrease of the relative yield value.
Since the shift towards the underdosed or overdosed state depends on the cement used, the differences occurring between cement C and the cements A, D, and E have to be regarded more in detail. It was shown that the superplasticizer adsorption behavior is strongly influenced by the content of C₃A and soluble alkalis of a single cement. With regard to these parameters, cement C differs much from the other cements (see Tab.3-5). Cement C is characterized by the highest C₃A content and by the lowest soluble alkali content. The soluble alkali content of the cements A, D and E is three to five times higher and the C₃A content is up to three times lower compared to cement C. As temperature increases, the content of sulfate and alkali ions was found to increase for the cements A, D, and E, but not for cement C (Fig. 4-9). In order to convert C₃A into ettringite, cement C needs much more sulfate ions compared to the other cements. Moreover, by increasing the cement paste temperature of cement C from 10 to 30°C, the ettringite content increased by about 50% (Fig. 4-32). This again increases the need of sulfates to convert C₃A into ettringite. But since the sulfate ion content remains constant, it is assumed that cement C is running short of sulfates at higher temperatures. As sulfate ions compete with superplasticizers for the reactive sites on the hydrating cement surface, it is concluded that the cement-superplasticizer system of cement C is shifting towards the underdosed state with respect to Na₂SO₄ addition. Due to the lower C₃A content of the cements A, D, and E and due to the increasing alkali sulfate content with temperature, it is concluded that the cements A, D, and E are shifting towards the overdosed state with respect to Na₂SO₄ addition.

**Fig. 5-15:** Relative yield value vs. temperature of the cements A, C, D and E and consequence of Na₂SO₄ addition (i.e. underdosed and overdosed state in terms of Na₂SO₄ addition). With regard to the rheological measurements, cement C is shifting towards the underdosed state, whereas the other cements are shifting towards the overdosed state. Minimal relative yield value is obtained at the Na₂SO₄-optimized state.
Finally, the influence of temperature is now discussed with regard to the presented model in Chap. 5.2.2, Fig. 5-12. Mortar temperature has a strong influence on the relative yield value due to changes in the dissolution kinetics of C₃A (i.e. reactivity of C₃A) and the sulfate containing cement phases. Although C₃A dissolution and the presence of sulfate ions are closely linked together (i.e. a higher C₃A reactivity needs more sulfate ions to be converted into ettringite), by increasing temperature two cases can be distinguished:

- **The influence of the increasing sulfate ion concentration is more important than the C₃A reactivity**

If the sulfate ion concentration is increased due to a better dissolution of sulfate containing phases, the same considerations as in Fig. 5-12 are valid: With increasing sulfate ion concentration, SP$_{ads}$ reaches a maximal value. Thus, by increasing temperature, such a system is shifting towards the overdosed state. This was found by Na$_2$SO$_4$ addition for the cements A, D, and E (see Fig. 5-15, to the right). Therefore, this behavior is assumed to be valid for the cements A, D, and E.

- **The increase of C₃A reactivity is more important than the sulfate ion concentration**

If the C₃A reactivity is increased, more superplasticizer molecules are incorporated in the hydration products (SP$_{inc}$); therefore, SP$_{inc}$ and SP$_{cem}$ increase, whereas SP$_{sol}$ decreases. The absolute sulfate ion concentration, at which SP$_{sol}$ reaches 100%, is increased. It follows that the amount of maximal SP$_{ads}$ is shifted towards higher sulfate ion concentrations (Fig. 5-16). Thus, by increasing temperature and constant sulfate ion concentration, such a system is shifting towards the underdosed state. This was found by Na$_2$SO$_4$ addition for cement C (see Fig. 5-15, to the left). Therefore, this behavior is assumed to be valid for cement C.
5. DISCUSSION

5.2.3.2 Cement B

At 20°C cement B shows a minimal relative yield value at 0.2 wt.-% Na$_2$SO$_4$ (Fig. 5-17). This means that the presented rheological model (Chap. 5.2.2) can also be applied to cement B. However, without Na$_2$SO$_4$, the cement-superplasticizer combinations of cement B show a maximal relative yield value at 20°C (Fig. 4-17). Therefore, the influence of temperature cannot be explained by a parabolic curve with a minimal relative yield value. Moreover, the influence of temperature cannot be explained as for the cements A, C, D and E in Chap. 5.2.3.1.

![Fig. 5-16: Influence of C$_3$A reactivity on the distribution of superplasticizers. Dotted lines represent the distribution at a lower C$_3$A reactivity, full lines at a higher C$_3$A reactivity. At higher reactivity, the maximal value of SP$_{ads}$ is shifted towards higher SO$_4^{2-}$ concentrations.]

![Fig. 5-17: Relative yield value of cement B vs. Na$_2$SO$_4$ addition.]

Cem B, w/c=0.35, 20°C
Up to now, the influence of temperature has been explained by superplasticizer adsorption, which is mainly governed by the C₃A reactivity and the sulfate ions present in the pore water. In the case of a very low C₃A content as present in cement B, other parameters might become more important. This might be for instance the superplasticizer adsorption on other cement or hydrate phases (e.g. adsorption on C₄AF, which is very high for cement B), temperature dependency of superplasticizer adsorption, morphology of the hydrates (e.g. ettringite, CSH-phases), particle size distribution of the cement, etc.

5.2.4 Limits of the Model

5.2.4.1 General Boundary Conditions

In general, the presented model in Chap. 5.2.2 is valid for:

- a defined cement with a constant C₃A content
- one superplasticizer at constant concentration (SPₜ₀ = const.)
- a constant mortar temperature

If mortar temperature is changed, two important parameters are affected: C₃A and alkali sulfates dissolution. Depending on the investigated cement, either the influence of C₃A dissolution or the influence of dissolved alkali sulfates might be more pronounced (see Chap. 5.2.3).

5.2.4.2 Superplasticizer Concentration

It has been shown in Chap. 4.2.3.2, Fig. 4-24 that due to the reduction of added superplasticizer the parabolic curve with its minimal relative yield value disappeared. Therefore, the mechanism of Na₂SO₄ addition is working as long as the superplasticizer concentration is above a certain concentration. If the system falls short of superplasticizer, the same behavior as found without superplasticizer is observed. It is assumed that the added superplasticizer content is almost fully incorporated in the hydration products. Therefore, the relative yield value is being adapted to the behavior as without superplasticizer.

5.2.4.3 Type of Superplasticizer

The presented rheological model in Chap. 5.2.2 is only valid for superplasticizers, which are significantly incorporated during the initial hydration reactions. Assuming only a negligible superplasticizer incorporation (SPinc ≈ 0) during the initial hydration period, mortar fluidity exclusively depends on the amount of SPads during the dormant period.
This is thought to happen for new types of PC superplasticizers. Experiments carried out by Hanehara support this assumption [135]. Assuming only a very low amount of $SP_{inc}$, there should not be a large difference in fluidity between direct and delayed superplasticizer addition. In fact, Hanehara only found a slight increase of the fluidity due to delayed superplasticizer addition. Thus, the used PC-type superplasticizer was not substantially incorporated into the initial hydrates. Moreover, the addition of Na$_2$SO$_4$ to the mixing water always provoked a decrease in fluidity, but never an increase. This is plausible, since fluidity only depends on $SP_{ads}$, which is given by the equilibrium between $SP_{ads}$ and $SP_{sol}$ and not on the amount of $(SP_{ads} + SP_{sol})$.

The PC superplasticizer in this work cannot be accounted to this group of superplasticizers. It is true that $SP_{cem}$ is lower compared to PMS or PNS (Fig. 4-5). However, $SP_{cem}$ is significant, which is confirmed by the experiments carried out by delayed addition (Fig. 4-23). Significant differences were found for the relative yield value between direct and delayed addition.

5.2.4.4 Time of Sulfate and Superplasticizer Addition

In this work the relative yield value has always been measured between the 15$^{th}$ and the 24$^{th}$ minute of profile A; but the water-soluble sulfates and the superplasticizers were added at the start of cement hydration ($t=0$min). During this time slot, the amounts of $SP_{inc}$ and $(SP_{ads} + SP_{sol})$ were changing. Therefore, both possibilities to increase $SP_{ads}$ have to be considered (see Chap. 5.2.1.1). If the amounts of $SP_{inc}$ and $(SP_{ads} + SP_{sol})$ do not change within the time slot from addition to measurement, $SP_{ads}$ is only affected by its equilibrium behavior with $SP_{sol}$ which is a function of SO$_4^{2-}$.

$SP_{inc}$ and the amount of $(SP_{ads} + SP_{sol})$ remain constant, if superplasticizers or sulfate ions are introduced during the dormant period. In these two cases, $SP_{inc}$ remains zero for the delayed superplasticizer addition or constant for the delayed sulfate ion addition. Therefore, an increase of the sulfate ion content lowers the fluidity during the dormant period (i.e. increases the relative yield value) due to the competitive superplasticizer adsorption.

5.2.4.5 Sulfate Source

It was shown for mortar without superplasticizers that the addition of Na$_2$SO$_4$ into the mixing water leads to a decrease of the relative yield value even at high Na$_2$SO$_4$ concentrations. This relation is schematically illustrated in Fig. 5-18a. Superplasticized mortars showed a minimal relative yield value (Fig. 5-18b). For superplasticized mortars only few data exist at high Na$_2$SO$_4$ concentrations (Fig. 4-19). However, it is assumed that the influence of superplasticizer is being superposed at high Na$_2$SO$_4$ concentrations as illustrated.
in Fig. 5-18c. This assumption is supported by the test series with cement A in Fig. 4-19.
After an increase up to about 2.0 wt.-% Na$_2$SO$_4$, the relative yield value decreased at higher concentrations. With respect to Fig. 5-18c, the measured values are thus located to the right of the minimal relative yield value. Moreover, with respect to the presented rheological model in Chap. 5.2.2, relative yield value would start to decrease as soon as no more superplasticizer molecules can be desorbed from the cement surface into the pore water due to a the very high sulfate ion content.

During the initial hydration period the influence of alkali sulfates on the total sulfate ion concentration was found to be larger compared to the one of calcium sulfates (Chap. 5.1.1.2). Therefore, dissolved Na$_2$SO$_4$ was added to the mixing water, assuming that the influence on the rheological properties is similar to the one of real alkali sulfates. However, sulfate ions originating from different sources (Na$_2$SO$_4$, K$_2$SO$_4$, Fe(II)SO$_4$·7H$_2$O) did not exhibit the same rheological behavior (Chap. 4.2.3.4). Similar results may be expected from real alkali sulfate phases as well. A possible reason may be the behavior of the cations (e.g. formation of insoluble iron salts, calcium hydroxides, etc.). Thus, deviations from the presented mechanisms are possibly to happen by varving the contents of real alkali sulfates.

5.2.4.6 Effect of Temperature

When regarding cement-superplasticizer combinations at different temperatures, the effect of the C$_3$A reactivity and the dissolved amount of the sulfate containing cement phases have to be considered. A higher C$_3$A reactivity provokes higher ettringite contents. As proposed by Nawa [127], an elevated ettringite content might be the cause of a decreased fluidity of superplasticized mortars due to an elevated water or sulfate ion consumption or due to the increased internal friction between the cement particles. However, in most of the experiments, this mineralogical influence is thought to be partially or fully superposed by the
dispersive force of the superplasticizers. Nevertheless, it has been mentioned that for the temperature characteristic of one cement-superplasticizer combination, (that is cement C-0.4 wt.-% PNS, see Fig. A-5 in the appendix), minimal relative yield value did not coincide with the optimized amount of Na$_2$SO$_4$. This system is optimized in terms of Na$_2$SO$_4$ at around 20°C, but the relative yield value was lower at 8°C. This might be explained by the ettringite content. Due to its increased amount at higher temperatures (i.e. at 20 and 30°C) the morphological influence increased at 20°C, which made the mortar less fluid at 20°C compared to 8°C. With regard to the high C$_3$A content of cement C, this influence is most possible to happen at cement C, since the amount of ettringite is higher compared to the other cements.

5.3 Summary of Cement-Superplasticizer Interactions with Regard to Relative Yield Value

Superplasticizers were found to interact with cement particles. Thereby, many complex interactions determine the rheological parameter relative yield value. The most important parameters were found to be temperature, C$_3$A dissolution, sulfate ion availability and superplasticizer adsorption behavior. Since the sulfate ion concentration in the pore water and the C$_3$A dissolution vary from one cement to another, it is very difficult to predict the superplasticizer adsorption behavior and the amount of SP$_{ads}$ (and thus the relative yield value)!

In Fig. 5-19 a general overview of these interactions is presented. Relative yield value was concluded to strongly depend on the adsorbed superplasticizer (SP$_{ads}$), which in turn was influenced by the C$_3$A content of cement and the sulfate ions present in the pore water.

Both C$_3$A dissolution and sulfate ion availability directly influence the relative yield value due to the formation of different types of hydrates (i.e. monosulfate, ettringite, secondary gypsum).

A higher C$_3$A dissolution leads to a higher superplasticizer incorporation (SP$_{inc}$) in the hydrates, which increases the relative yield value. With regard to the superplasticizer adsorption mechanism, sulfate ions in the pore water reduce the amount of SP$_{inc}$ and they reduce the amount of SP$_{ads}$ during the dormant period. It depends on the sulfate ion content in the pore water, whether the relative yield value increases or decreases. These relations are discussed in Chap. 5.2.2 by means of a rheological model based on superplasticizer adsorption.
It has been shown that temperature may also have a large influence on the rheological properties of superplasticized mortars or concretes. This happens due to a change in the dissolution kinetics of C₃A and the sulfate containing cement phases. The C₃A dissolution of cement C was assumed to increase due to an elevated ettringite content at higher temperatures. Apart from cement C, the sulfate ion concentration increased with increasing temperature for the cements A, B, D, and E (Fig. 4-9).

![Diagram](image_url)

**Fig. 5-19:** Schematic illustration of the cement-superplasticizer interactions.
6 CONCLUSIONS

6.1 General Conclusions

A large number of rheological experiments have been performed by using a rotational viscometer, which allows more scientific parameters to be derived compared to simple slump or slump flow tests. The rheological parameters relative yield value, relative viscosity coefficient and stiffening value provided ample information about the rheological behavior within the first hour of cement hydration (Tab. 4-5). Relative yield value was found to have a very complex and sensitive behavior, whereas the relative viscosity coefficient and the stiffening rate provided more simple results and trends. Pore water and cement phase analyses completed these information. Moreover, a comparison between results made on mortars and concrete showed that the transferability of results from mortar to concrete was possible in most of the cases. It is of practical relevance that the relative yield value can be correlated with the slump or slump flow, since most of the fluidity tests in the practice are based on slump or slump flow tests. This is not the case for the relative viscosity coefficient, since it cannot easily be correlated to another fluidity parameter.

The behavior of superplasticized cement was very much influenced by the type and amount of superplasticizer used, by the composition of the cement, and by environmental conditions (i.e. mortar temperature). Pore water analysis showed that the superplasticizer adsorption behavior mainly depended on the amount and reactivity of C₃A (Fig. 4-4). The more C₃A a cement contained, the higher the adsorbed and incorporated superplasticizer content (=SP_cem) was. By the addition of Na₂SO₄ into the mixing water SP_cem was reduced significantly (Fig. 4-6). Hence, sulfate ions played an important role in the adsorption behavior of superplasticizers.
Sulfate ions in the pore water originate from sulfate containing cement phases, which are calcium sulfates and alkali sulfates. The content of alkali sulfates can be expressed in terms of the soluble alkali content in cement. The soluble alkali content increased with temperature, as did the sulfate ion concentration (Fig. 4-9). Since calcium sulfate phases (i.e. dihydrate, hemihydrate, anhydrite) are less soluble compared to alkali sulfates, the latter have a large influence on the total sulfate ion content in the pore water. When water was present in excess (experiments made at a w/c of 50), more than two third of the alkali sulfates get dissolved during the initial hydration period (Chap. 5.1.1.1). It is therefore concluded that alkali sulfates are for the most part located at the surface of the cement particles or exist as monomineralic particles and are highly soluble in the presence of water. Even at a low w/c ratio of 0.35, the dissolved amount was only reduced by maximal 25%, which means that at least 55% of the alkali sulfates were dissolved.

Although it is known that the initial hydration of C₃A has a large influence on the initial fluidity, it is often difficult to find a correlation between these two parameters. As a result of quantitative determination of cement phases by using QXRD, it was possible to correlate the relative yield value with the C₃A content and the cement fineness of cement pastes made without superplasticizers (Fig. 5-4). Thereby, the fineness played a secondary role compared to the C₃A content. For superplasticized mortars, very good to very poor correlations were obtained depending on the dosage of the superplasticizer used. Although large variations were detected from cement to cement, stiffening rate did not correlate with the C₃A content, as might be expected at first glance.

The initial fluidity of a superplasticized cement paste system is assumed to be governed by the superplasticizer content adsorbed on the cement particle surface (SPₐds). This content mainly depended on the sulfate ion content present in the pore water, on the content of C₃A of the cement, and on the superplasticizers tendency to get incorporated in the initial hydration products. According to these relations, the minimal relative yield value, which is often found when soluble Na₂SO₄ is added to the mixing water, was explained in terms of a superplasticizer adsorption mechanism (Chap. 5.2.2).

In this work DSC analysis showed that the addition of Na₂SO₄ to a superplasticized cement system did not yield to a qualitative change in the composition of the hydration products ettringite, monosulfate and calcium sulfate dihydrate (i.e. secondary gypsum) (Chap. 4.3, Fig. 4-34). It is therefore concluded that the observed parabolic curve having a minimal relative yield value is not caused by an improper conversion from C₃A into its hydration products, but by the dispersive force of the superplasticizers.

Mortar temperature was found to have a strong influence on the rheological parameters, on the pore water chemistry, and on the ettringite formed. The results made at different temperatures (i.e. 8-30°C) showed that every cement-superplasticizer combination had its
own temperature characteristic with respect to relative yield value. The impact of Na$_2$SO$_4$ was different at different temperatures. However, the behavior of the relative yield value of the cements A, C, D and E could be explained by the above-mentioned superplasticizer adsorption mechanism, taking into account the effects of temperature on the dissolution kinetics of C$_3$A and alkali sulfates.

6.2 Recommendations of Practical Interest

6.2.1 C$_3$A Content

The rheological experiments showed that the content of C$_3$A is related with the relative yield value of freshly mixed cement paste or mortar. The relative yield value, which can be compared with the reciprocal value of the slump or slump flow (i.e. the higher the relative yield value, the lower the slump/slump flow), increases with increasing C$_3$A content and cement fineness. However, the correlation is not that good that the slump flow for cements originating from different cement plants are predictable on the basis of its C$_3$A content. But nevertheless, the comparison between the two cements from the same cement plant confirmed that the correlation is much better, if parameters like raw materials, fuels and burning conditions remain similar or constant (Chap. 5.1.2.1, Fig. 5-2). Therefore, a specific variation of the C$_3$A content in a cement plant will have a direct consequence on the relative yield value and on the initial slump and slump flow. Very high C$_3$A contents will negatively affect the initial flow behavior of concrete.

6.2.2 Superplasticizer Adsorption

Another direct effect of the C$_3$A content is the superplasticizer adsorption behavior. It was shown that the higher the C$_3$A content, the higher the initial superplasticizer adsorption. This signifies that a cement with a low C$_3$A content needs less superplasticizer for the same initial fluidity. This might reduce the costs of superplasticizers needed by up to 50% per cubic meter.

6.2.3 Alkali Sulfates

If the sulfatisation degree of the cement is high, sulfates and alkalis mainly form alkali sulfates, otherwise the remaining components (i.e. alkali or sulfate ions) are incorporated into other clinker phases. This alters the hydration behavior of the clinker phases. Alkali sulfates provide a substantial amount of soluble sulfates very soon after the contact with water. With
regard to the initial fluidity of mortar or concrete, it is assumed that the addition of (natural) gypsum as set regulators (i.e. calcium sulfate dihydrate, hemihydrate and anhydrite) is not always necessary. This is explained by the fast dissolution rate of the alkali sulfates even at low w/c ratios such as 0.35. These phases may provide enough sulfate ions for the initial ettringite formation. The consumption of calcium ions is thought to be sufficiently provided by the initial dissolution reactions and the hydrolysis of cement particles (Chap. 2.4.2.1). During the first hour of cement hydration about 5 to 15% of the total C₃A content is reacting. Therefore, calcium sulfates are still needed for the subsequent hydration of the remaining 85-95% C₃A. This information implies that the amount of fast dissolving calcium sulfates (i.e. hemihydrate, technical anhydrite) might be reduced. This can be achieved for instance by a clinker grinding temperature below the dehydration temperature of calcium sulfate dihydrate (i.e. 70-80°C) or by the use of natural anhydrite as set regulator.

6.2.4 Quantitative X-Ray Diffraction

The cement manufacture process is very complex. By varying for instance the burning and cooling history at a constant chemical input of the raw materials, the phase composition of the clinker is modified. A simple Bogue calculation of the main cement phases is not able to take this into account. Hence, in order to have a better quantification of the cement composition, quantitative X-ray diffraction has to be chosen instead of the Bogue-formula [130-132]. Good quantitative XRD results can be obtained, when the cement is analyzed without C₃S and C₂S (see SAL-method, Chap. 3.2.5). By applying this procedure, the minor cement phases can be determined without the overlapping peaks of C₃S and C₂S and thus the calculation of the total cement phase content by the Rietveld method is more accurate.

6.2.5 Test Procedure for the Evaluation of Cement–Superplasticizer Interactions

How does a rheological test have to be performed so that the cement-superplasticizer compatibility can be investigated and how can this information be used to make superplasticized concrete? In Fig. 6-1 a guideline for the making of superplasticized concrete is shown. Due to the findings of this work, the following procedure is proposed:

Choice of a cement-superplasticizer combination and a w/c ratio

- Due to the desired specification of the concrete, one or preferentially various cement-superplasticizer combinations are selected at the desired w/c ratio.
Determination of the superplasticizer saturation dosage (SP\textsubscript{sat})

- Superplasticizer saturation dosage (see Chap. 4.2.2.1) is determined at 20°C (or at room temperature) by using a rotational viscometer. The superplasticizer concentration is increased at allotted steps until bleeding and segregation of the mortar occurs. If no rotational viscometer is available, SP\textsubscript{sat} has to be determined by a slump or slump flow test.

Temperature dependency

- At a concentration > 50% of the superplasticizer saturation dosage, the effect of temperature (10-30°C) is measured. Concentrations below 50% SP\textsubscript{sat} (~10-20% of SP\textsubscript{sat}) might lead to a disappearance of the cement-superplasticizer interactions. In this case, the same temperature dependency as without superplasticizer is assumed.

Acceptance or refutation of the investigated cement-superplasticizer combinations

- If various cement-superplasticizer combinations were analyzed, one combination can be accepted due to its superplasticizer adsorption behavior or due to its temperature dependency. If for instance the temperature dependency is assumed to be too high, a new cement-superplasticizer combination has to be chosen and analyzed.

Determination of the superplasticizer saturation dosage (SP\textsubscript{sat}) of concrete

- Now, the superplasticizer saturation dosage of the concrete is evaluated at room temperature by using a simple slump test (or a similar flow test).

Adjusting fluidity

- Practically, for maximal fluidity the addition of superplasticizer has to be limited to up to 80-85 wt.-% of SP\textsubscript{sat} (determined at room temperature). This is suggested due to the fact that SP\textsubscript{cem} may vary depending on the concrete temperature. If less superplasticizer is adsorbed compared to room temperature, more superplasticizer remains in solution and segregation could occur. This, however, is impeded by the suggested superplasticizer dosage, which is significantly below the saturation dosage. If more superplasticizer is adsorbed than expected, fluidity is lower. In this case, a small quantity of superplasticizer (5-10% of the segregation dosage) can be added to the freshly mixed concrete without risking segregation. It has to be noted that, if the added superplasticizer concentration is low (i.e. slump or slump flow is only slightly reduced), maybe the stiffening is increased relative to the same concrete made without superplasticizer (see Fig. 4-22c).
Segregation

- In the case of segregation due to a too high superplasticizer concentration further mixing by some minutes may resolve the problem. Otherwise, the addition of sand or a cohesive agent might be useful.

Fig. 6-1: Guideline for the use of superplasticized concrete at various temperatures.
6. Conclusions

6.3 Outlook

In this work, cement-superplasticizer interactions at a water to cement ratio of 0.35 were found to depend on the contents of C₃A, soluble alkali sulfates and temperature. Sulfate ions played an important role with regard to the adsorption behavior of superplasticizers and therefore for the flow behavior of mortar or concrete as well. However, different kinds of commercial sulfates did not yield the same rheological parameters. Therefore, it would be favorable to investigate more in detail the influence of different types of alkali sulfates (arcanite, aphthitalite, Ca-langbeinite) on the adsorption behavior of superplasticizers and on the rheological parameters of mortar.

It is the purpose to correlate fluidity of mortar with parameters, which can be deduced from the starting materials (e.g. mineralogical or chemical composition of the cement, cement fineness, etc.). Relative yield value was found to be correlated with the C₃A content and the cement fineness. However, the obtained correlation coefficients (r² < 0.83 with, and < 0.65 without superplasticizer) were still far from one. Therefore, further parameters have to be considered as for instance:

- **C₃A reactivity.** C₃A dissolution does not only depend on its content, but also on its reactivity. At constant temperature, this parameter is mainly influenced by the crystal modification of C₃A and by the incorporation of foreign ions (Na⁺, K⁺, SO₄²⁻).

- **Phase composition of other cement main phases.** It was shown that the correlation coefficient between cement parameters and relative yield value increased for mortars made without superplasticizers, if the amount of C₂S is considered besides C₃A and cement fineness. It has to be clarified, whether this is a real or a random relation.

- **Minor cement phases.** Sulfates are needed to convert C₃A and gypsum into ettringite. If the sulfates are not adjusted to the reactivity of C₃A, the formation of other hydrates (monosulfate, secondary gypsum) might influence the flow behavior.

- **Particle size distribution.** The particle size of various cements having the same cement fineness according to the Blaine value can be different. By this means, the flow behavior might be affected due to different packing densities or different cement phase reactivities.

- **Superplasticizer adsorption behavior.** Due to the lack of more specific data (e.g. dissolved amount of different cement phases, amount of ettringite, monosulfate, CSH-phases), superplasticizer adsorption was attributed to C₃A. However, different cement phases or hydrates adsorb different amounts of superplasticizers.
What has to be defined is how these parameters should be investigated. For a proper cement phase analysis, quantitative X-ray diffraction is suggested. Phase calculation according to the Bogue-formula is thought to be insufficient for this purpose. Different dissolution techniques (e.g. SAL-method) enrich the minor cement phases. Hydrates might be detected by DSC. The influence of different cement phases may be analyzed by:

- adding laboratory-made cement phases to a laboratory-made cement
- adding laboratory-made cement phases to a commercial cement
- commercial cements by determining its minor phases by QXRD

Further research is needed to validate both the superplasticizer adsorption mechanism as a function of the sulfate ion concentration and the resulting fluidity. The influence of temperature on the relative yield value could not be fully explained, especially for cement B. A promising way to do this would be to contemporaneously analyze different cement paste systems with different test methods at the same time (e.g. rheological parameters, pore water ($C_{org}$, $SO_4^{2-}$), cement phase analyses (QXRD, DSC)). In addition to rheological experiments, the determination of the strength development would give an indication on the behavior in hardened state.
7 REFERENCES


7. REFERENCES


7. REFERENCES


Fig. A-1: XRD diagrams of the cements A, B, C and D.
Fig. A-2: XRD diagrams of the cements E, F, G, H, I and K.
Fig. A-3: Relative yield value vs. superplasticizer dosage ("saturation curve"), cements A, B, C, D, E.
Fig. A-4: Relative viscosity coefficient vs. superplasticizer dosage, cements A, B, C, D, E.
8. APPENDIX

Fig. A-5: Influence of 0.4 wt.% Na$_2$SO$_4$ addition on the relative yield value for the cements C, D, E. 0.2 wt.% Na$_2$SO$_4$ was added to cement B.
Fig. A-6: Stiffening values of the cement-superplasticizer combinations, cements A, B, C, D, E.

Fig. A-7: Effect of delayed addition to the relative yield value and the relative viscosity coefficient. The starting point of the arrowas represent the situation at direct addition, while the spike of the arrow represents the situation at delayed addition.
Fig. A-8: Relative yield value as a function of different cement parameter: a) C₃A, b and d) C₃A*Blaine, and c) (C₃A+CaS)*Blaine.
Fig. A-9: Cement characteristics and rheological parameters. The different parameters are plotted in relative units.

Fig. A-10: Difference in relative yield value between cements with and without Na₂SO₄ addition. Negative values indicate a decrease in yield value by adding Na₂SO₄. For cement C the values are shifted towards the negative direction (downward arrow). Other cements A, C, D, and E are shown in Fig. 5-14.
ACKNOWLEDGMENTS

First of all I would like to thank Prof. Dr. H. Böhni for the scientific support of this work. It was a stroke of luck that just at the end of my studies a person was searched in order to pursue and end this work. In this regard I would like to thank Dr. A. Stahel for his "job placement". I am much obliged to the whole staff of the IBWK. Although I was not "always" present at the institute, I did not become a stranger. Thanks Dr. M. Plötze and Dr. G. Kahr for assisting me by quantifying the cement phases.

Thank you Dr. P.-C. Nkinamubanzi for the great time I had during my short stage at the University of Sherbrooke, Canada.

Thank goes to the company TFB and to all persons working there. They supported my thesis by providing the measuring equipment and by technical assistance. I am much obliged to Dr. F. Hunkeler and Dr. F. Jacobs for the numerous discussions, which increased my knowledge about cement and concrete continuously.

I would like to thank Prof. Dr. H. Hofmann (LTP at EPFL) for agreeing to be co-examiner of this work.

I would also like to thank the Swiss cement industry ("Stiftung für angewandte Forschung im Betonbau") for its financial support. Special thank goes to the employees of the Swiss cement plants, which were involved in this work.

Last but not least a cordial thank you to my family, especially to my parents and to my girlfriend Carine, who supported me during my studies.
CURRICULUM VITAE


1999-2002  Ph.D and teaching assistant at the Institute of Building Materials, Material Chemistry and Corrosion (IBWK) at the Swiss Federal Institute of Technology, Zurich (ETH-Zurich) in collaboration with the company Technical Research and Consulting on cement and Concrete (TFB, Switzerland)


1999  Swiss Federal Maturity, Type B; MARS Zurich

PUBLICATIONS
