

The influence of superplasticizers on the hydration of Portland cement

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Abstract

The investigation of the solid and liquid phase of hydrating Portland cement in the absence and presence of a polycarboxylate-based superplasticizer (PCE) showed that the superplasticizer retarded during the first 30 hours the dissolution of alite strongly, thus delaying the formation of portlandite and C-S-H. The retardation of ettringite formation was less distinct. After 6 days no significant difference in the amount of the different hydrates formed was observed.

After 1 hour, about 50 % of the PCE added was still dissolved. Only very little further uptake of PCE was observed. No significant complex formation between PCE and dissolved ions such as Na, K, Ca, or Al was observed in the pore solution of hydrating cements between one hour and 300 days, indicating that the retarding and plasticizing effect of PCE is not due to interactions with dissolved Ca^{2+} or other ions but rather based on steric (and electrostatic) dispersion mechanisms and on their sorption on solid phases present.

1 Introduction

Superplasticizers (SP) are nowadays commonly used in concrete technology to improve the workability of cementitious systems. They are adsorbed on the cement particles and act as dispersants by electrostatic and/or steric repulsion effects as demonstrated by Uchikawa et al. [1]. Among the various kinds of superplasticizers, new generation polymers with enhanced properties based on comb-shaped polycarboxylate ethers are increasingly applied.

The workability of cement based materials containing superplasticizers depends on various parameters. On one hand, the type, the chemical composition and the molecular structure of the admixture influence the rheology [2-4]. On the other hand, the chemical composition of the cements, especially the amount of C_3A and the availability of sulphate during early hydration affects the performance of superplasticizers [4-6]

The composition and development of the aqueous phase during cement hydration gives an important insight into the chemical processes and the interactions between liquid and solid phases as well as into the fate of SP. Little investigations deal with the influence of plasticizers on the composition of the pore solution and none concerning the interaction between pore solution and polycarboxylate based superplasticizers. Schwarz [7] observed a strong influence of citrate and carbonate on the

composition of the pore solution of hydrating cements. The presence of sodium naphthalene sulphonates has been observed to increase the sodium and, to a lower extent, also the sulphate concentrations during the first two hours [8, 9].

The thermodynamic modelling of the interactions between the solid and liquid phase in cements using geochemical speciation codes can be the basis for the chemical understanding of these processes and of the factors influencing them. Thermodynamic modelling can also be used to study the chemical influence of composition and admixtures on the hydrate assemblage as well as on the composition of the pore solution. Lothenbach and Winnefeld [10] and Lothenbach and Wieland [11] coupled thermodynamic modelling with a set of simple equations to describe the kinetics of cement hydration and were thus able to predict quantitatively the composition of the solid and liquid phase at 20 °C.

In this paper, the impact of a polycarboxylate based SP on the hydration of OPC was explored by calorimetry and rheology. The composition of the solid and liquid phase was investigated as a function of time and the uptake of the SP during hydration was examined. In addition, the hydration of the OPC was calculated by thermodynamic modelling using the thermodynamic model developed by Lothenbach and Winnefeld [10]. Comparison with experimental results served to quantify the influence of the superplasticizer on the chemistry of the pore solution.

2 Experimental

2.1 Materials and methods

All experiments were carried out using an ordinary Portland cement (OPC), CEM I 42.5 N, at 20° C (cf. Table 1). The chemical composition of the polycarboxylate-based superplasticizer (PCE) was determined by ICP-OES and TOC-Analyzer, its solid content according to EN 480-8 (heating of 2 g of superplasticizer for 4 hours at 105°C): solid content: 312 g/kg, TOC: 140 g/kg; Na: 13 g/kg, S: 9 g/kg; P: 3 g/kg; K 0.2 g/kg, Ca 0.01 g/kg, Al, Ba, Cr, Fe, Li, Mg, Mo, Rb, Si, Sr < 0.01 g/kg. All dosages of superplasticizer given in this paper refer to the aqueous solution as delivered.

Cement pastes were prepared with a w/c of 0.4 by adding cement to distilled water. To one series of experiments 0.4 wt.-% (referring to the weight of cement) of PCE was added to the water. The pastes were cast in PE-bottles, sealed tightly to exclude the ingress of CO₂ and the evaporation of water and stored at the appropriate temperature. After different reaction times, the pore solutions of cement samples were either collected by vacuum filtration (hydration time <7 hours) or by using the steel die method and pressures up to 530 N/mm² (hydration time >7 hours). The solutions were immediately filtered using 0.45 µm nylon filters. After filtration an aliquot was diluted with HNO₃ (6.5%) to prevent the precipitation of solid phases. The remaining solution was used for pH measurements. The pH electrode was calibrated using KOH solutions of

known concentrations. The total concentrations of the Na, K, Ca, Al, S, and Si were determined using inductively plasma optical emission spectroscopy (ICP-OES), total organic carbon (TOC) using a TOC-analyzer. The solid fractions of the cement paste were crushed and ground in acetone, dried at 40 °C and then used for XRD and thermogravimetric analysis (TGA). TGA was carried out in N₂ on about 10 mg of powdered cement pastes at 20 °C/min up to 980 °C.

Table 1: Composition of CEM I 42.5 N. Blaine surface area: 300 m²/kg.

Chemical analysis		phase composition ⁱⁱ	
	g/100g		g/100g
SiO ₂	19.7	alite	55
Al ₂ O ₃	4.7	belite	15
Fe ₂ O ₃	2.67	aluminate	7.9
CaO	63.2	ferrite	8.1
MgO	1.85	CaO	0.46
SrO	0.07	CaCO ₃	4.4
K ₂ O	1.12	CaSO ₄ ⁱⁱⁱ	4.2
Na ₂ O	0.08	K ₂ SO ₄ ⁱ	1.6
CaO (free)	0.46	Na ₂ SO ₄ ⁱ	0.096
CO ₂	1.93	SrO	0.07
SO ₃	3.35	K ₂ O ^{iv}	0.26
<i>readily soluble alkalisⁱ</i>		Na ₂ O ^{iv}	0.04
K ₂ O	0.86 (77% of K _{tot})	MgO ^{iv}	1.9
Na ₂ O	0.042 (52% of Na _{tot})	SO ₃ ^{iv}	0.12

ⁱ readily soluble alkalis were calculated from the concentrations of alkalis measured in the solution after 5 minutes agitation at a w/c of 10. ⁱⁱ calculated from the chemical analysis. ⁱⁱⁱ present as anhydrite (2.5 g/100g), hemihydrate (0.5 g/100g) and gypsum (1.5 g/100g). ^{iv} present as solid solution in the major clinker phases.

For the rheological experiments a Paar Physica MCR 300 rheometer was used. A cylindrical measuring geometry according to ISO 3219 with a cup and a rotating bob (measuring gap 1.13 mm, ratio outer/inner radius 1.08, serrated surface with a depth of 100 µm) was applied. 50 g of cement was blended with water or the admixture containing solution for two minutes by hand using a spatula. The superplasticizer dosage was increased in steps of 0.1% until the apparent yield stress dropped below 1 Pa. The measurement started 5 minutes after water or the admixture containing solution was added to the cement; the measuring temperature was kept constant at 20°C. After one minute of pre-shearing at a shear rate of 100 s⁻¹, a flow curve with shear rates between 100 and 0.1 s⁻¹ was recorded. Apparent yield stress and plastic viscosity were calculated according to the Bingham model. A conduction calorimeter (Thermometric TAM Air)

was used for the determination of the rate of hydration heat liberation. The mixing was done by a small stirrer for two minutes. The flask was then capped and placed into the calorimeter. The heat flow was recorded for 72 hours; measuring temperature was 20°C.

2.2 Modelling

The hydration model used in this study is described in detail by Lothenbach and Winnefeld [10]. The composition of the solid and liquid phase as a function of time and temperature is calculated based (i) on the measured composition of the cement paste as given in Table 1, (ii) on the calculated dissolution rates of the clinker phases (see [10, 12]) as kinetic input and (iii) on thermodynamic calculations using a consistent thermodynamic dataset [10]. In the case of OPC with PCE, the composition of PCE as measured (140 g TOC/kg, 40 g Na₂SO₄/kg) was taken into account.

3 Results

3.1 Influence of PCE on rheology and heat of hydration

The results obtained for apparent yield stress and plastic viscosity are given in Fig. 1. At dosages of 0.4% PCE (for w/c 0.40) and 0.5% PCE (for w/c 0.35) the rheological saturation point (yield stress ≈ 0 Pa, segregation of cement particles) is reached. The applied dosage of 0.4% SP in the hydration experiments with w/c = 0.40 corresponds to the rheological saturation point. Therefore a surplus of admixture in the pore solution can be expected.

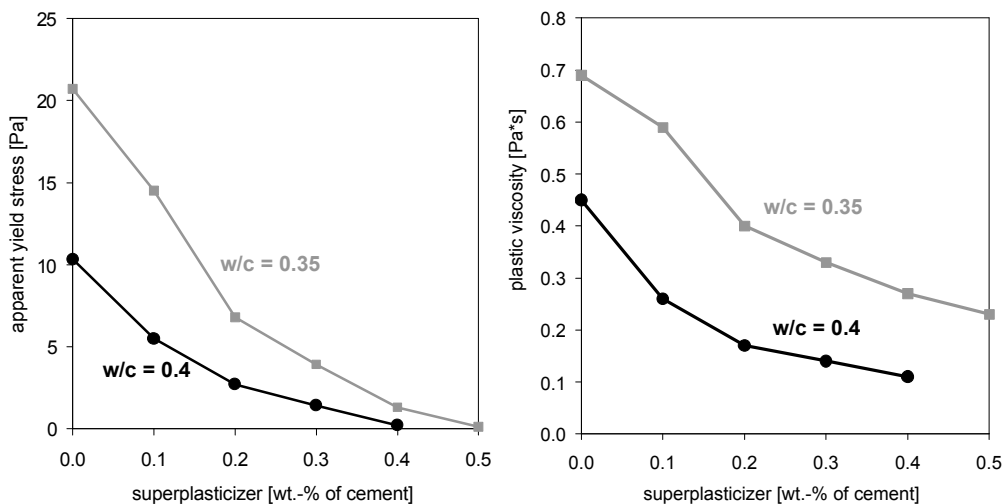


Fig. 1: Apparent yield stress (left) and plastic viscosity (right) of OPC - pastes with various amounts of PCE

The retarding effect of the PCE on OPC hydration is displayed in Fig. 2. The maximum of the main hydration peak of OPC referring to C_3S -hydration is shifted from 10 h without admixture to 16 h with 0.4% PCE. The third maximum or shoulder (depletion of sulphate) is shifted from 14 h to 18 h of hydration. The total heat release of the PCE containing sample exceeds after 35 hours the heat release of the sample without PCE.

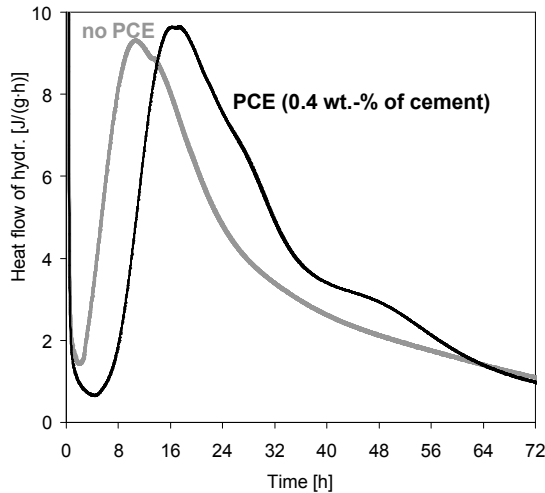


Fig. 2: Heat flow development of OPC paste with and without PCE

3.2 Solid phases

In the common understanding of Portland cement hydration, the term hydration comprises both the hydration of the anhydrous clinker phases as well as the formation of hydrates. The extent of the dissolution of the clinker phases is estimated based on the changes in the peak intensities of the crystalline phases in XRD patterns while the formation of hydrates is observed by both XRD and TGA/DTG. The XRD patterns show that during the first day less alite is dissolved in the presence of PCE than in its absence. Accordingly the formation of portlandite is observed to start later in the presence of PCE. Both these observations illustrate the retarding effect of the PCE during the first day which is in agreement with the calorimetric data presented above and observations reported in the literature (e.g. [4]).

The TGA data in Fig. 3 show that after 6 hours the formation of portlandite was observed in the absence of PCE. In the system with PCE, no portlandite has formed at this time. Up to 30 hours, less portlandite is found in the systems with PCE due to the retarding effect of the PCE. However, after 6 and more days no significant difference in the amount and kind of hydration products formed has been observed. Also the formation of ettringite is retarded after six hours. After 16 hours, however, no relevant difference in the amount of ettringite formed is observed

between the pastes containing PCE or no PCE. Puertas et al. [13] observed after a hydration time of 2 and 28 days that the presence of a polycarboxylate-based SP induced no significant mineralogical modifications but slight changes in the precipitating C-S-H. An initial retardation of ettringite and portlandite formation has been reported for naphthalene sulphonate- and lignosulphonate-based SP [9, 14].

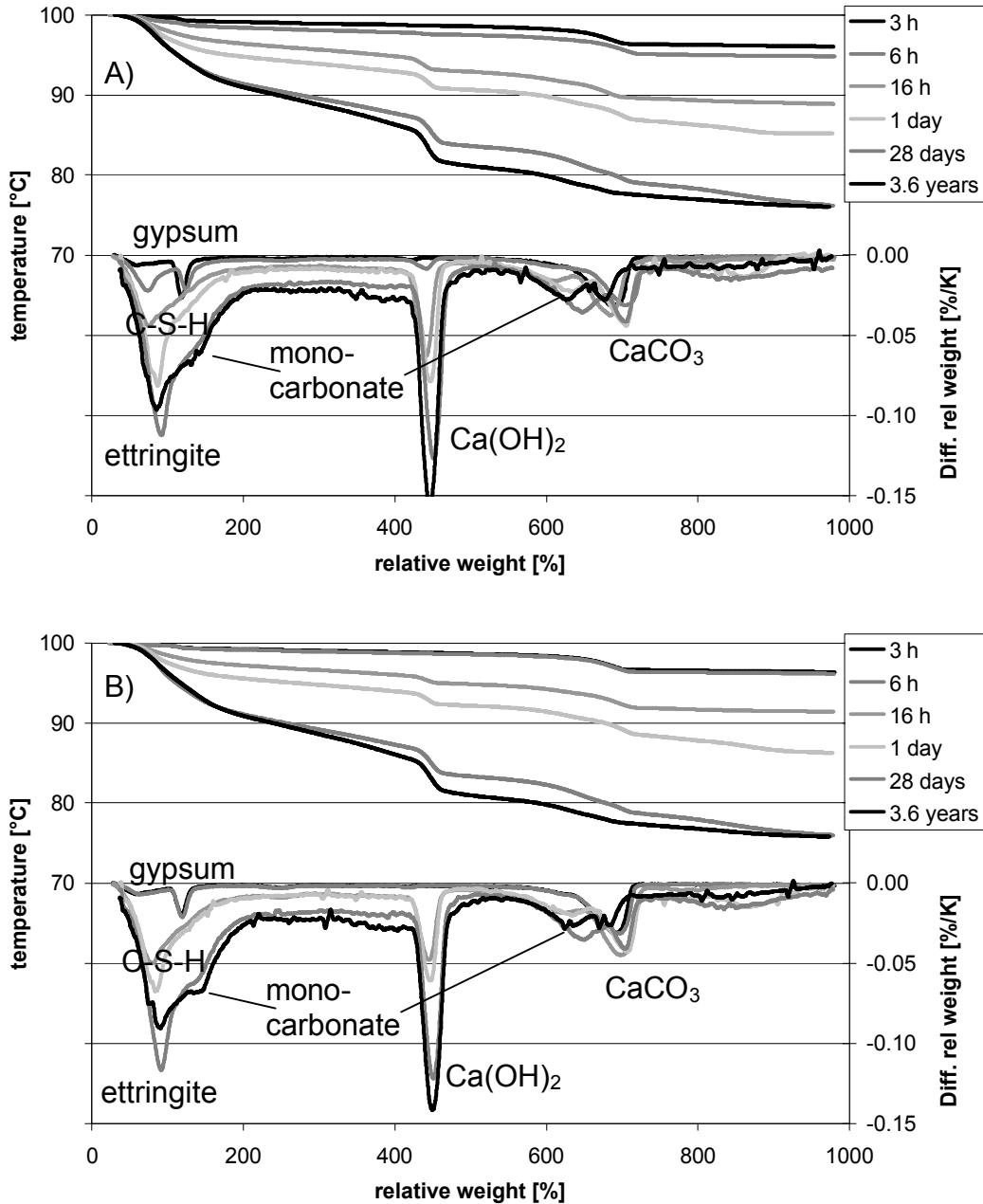


Fig. 3: TGA/DTG of OPC A) without the addition of SP and B) with 0.4 wt% of PCE.

3.3 Liquid phase

During the first hours of the hydration process the composition of the pore solution of the OPC in presence and absence of PCE is dominated by OH^- , K, Na, Ca and S(sulphate) (Fig. 5). During the first 12 hours, the composition of the pore solution is more or less constant. The concentrations of S and Ca are limited by the presence of portlandite and gypsum. Due to the precipitation of ettringite, gypsum and anhydrite are consumed with time and the sulphate concentration decreases drastically between half a day and a day of hydration. At the same time, OH^- concentrations increase, as the electroneutrality of the solution is maintained. The increase of pH leads to a lower Ca and higher Al concentration. A more detailed discussion of the hydration of OPC is given in Lothenbach and Winnefeld [10].

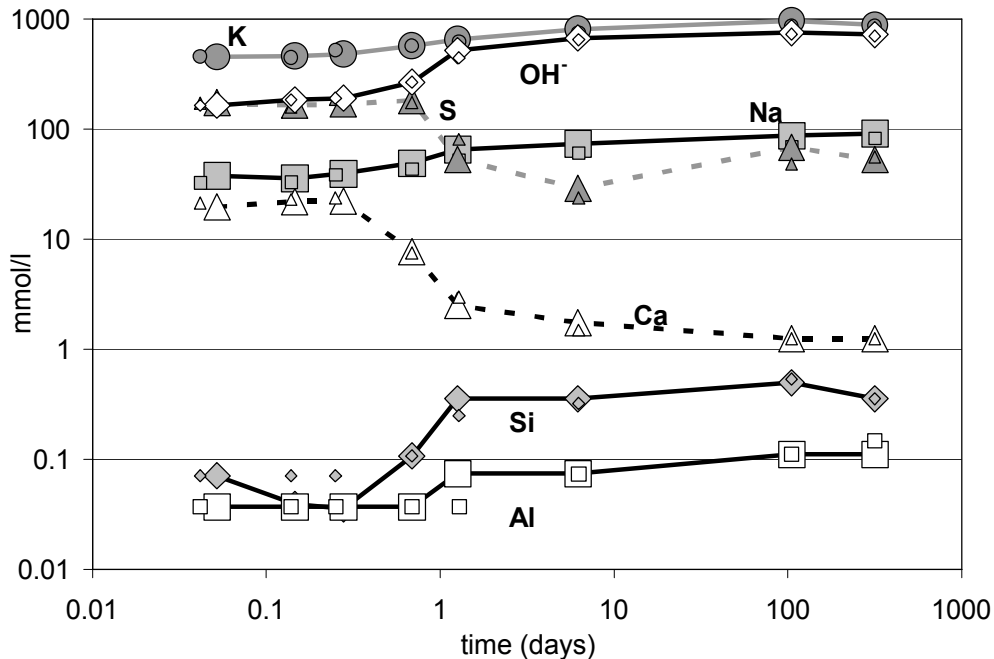


Fig. 4: Measured concentrations in the pore solution as a function of time of hydration. Large symbols refer to concentrations in the pore solution with PCE; small symbols give the concentration in the absence of PCE. Lines are intended as eye guides only.

The presence of polycarboxylate based PCE had neither an influence on the concentrations measured in the pore solution nor on the observed trends. The only observable difference was a slight increase in Na concentrations by about 10 % in the presence of PCE, which is due to the Na present in the PCE itself (PCE contains 13 g Na/kg). The agreement between the concentrations measured in the pore solution in the absence and presence of PCE indicates that no significant complexation occurs between the polycarboxylate-based superplasticizer and the ions present

in the pore solution. This agrees with findings of Richter and Winkler [15] and the references given therein who reported low stability constants of $10^2 - 2 \cdot 10^5$ for complexes between Ca^{2+} and polyacrylic acid. According to Mollah et al. [6] other mechanisms than complexation of Ca^{2+} might be responsible for the alite retardation: (i) adsorbed superplasticizers prevent the diffusion of water and calcium ions at the cement-solution interface, (however, adsorption on C_3S is much less compared to C_3A [16]), (ii) the dispersive action of superplasticizers changes growth kinetics and morphology of hydrate phases. The strong sorption of polycarboxylate-based superplasticizers on aluminate and its hydration products [16] does not seem to hinder its dissolution. Our findings confirm further that the effects of polycarboxylate-based superplasticizers concerning rheology and impact on hydration kinetics (retardation) are based rather on steric (and electrostatic) dispersion mechanisms [1] and on their sorption on solid phases present than on chemical interaction with the dissolved ions.

The presence of PCE does also not influence the concentration of aluminium and sulphate in the pore solution and does also not change the time when sulphate and calcium concentrations decrease and hydroxide concentrations increase. This indicates that even though ettringite formation is initially somewhat retarded in the presence of PCE (Fig. 3), after 16 hours and more an identical amount of aluminate (and possibly ferrite) has dissolved and precipitated as ettringite.

During the first hour, 55 % of the PCE added was taken up by the solid phases (Fig. 5), i.e. 0.7 mg per g cement, referring to the solid content of PCE or 0.3 mg per g cement, referring to TOC. This is relatively low percentage of PCE taken up is due to high dosage of PCE used (cf. Fig. 1). Generally, the uptake of PCE by solid phases during workability time has been observed remain constant (e. g. [3, 4]) or to increase (e. g. [17]) depending on the type of the polymer and the composition of the cement. C_3A and C_4AF and their hydration products adsorb PCE to a much higher extent than the silicate phases [16]. Strictly speaking “adsorption” is not the correct term, as a part of the consumed polymer is probably irreversibly coprecipitated with early cement hydration products like monosulphate and C_4AH_x and thus not effective for dispersion [5]. This is especially the case when not enough soluble sulphates are available to react with C_3A to ettringite during the very early hydration.

With increasing hydration time the concentrations of organic carbon in the pore solution increases (Fig. 5). This rise in total organic carbon is not due to a release of PCE during hydration but corresponds to the decrease of the amount of pore solution present in the system (see also section modelling below) resulting in higher concentrations in the remaining solution. A similar increase of organic carbon in the pore solution after longer hydration times has been reported for naphthalene sulphonate- and lignosulphonate-based superplasticizers [18].

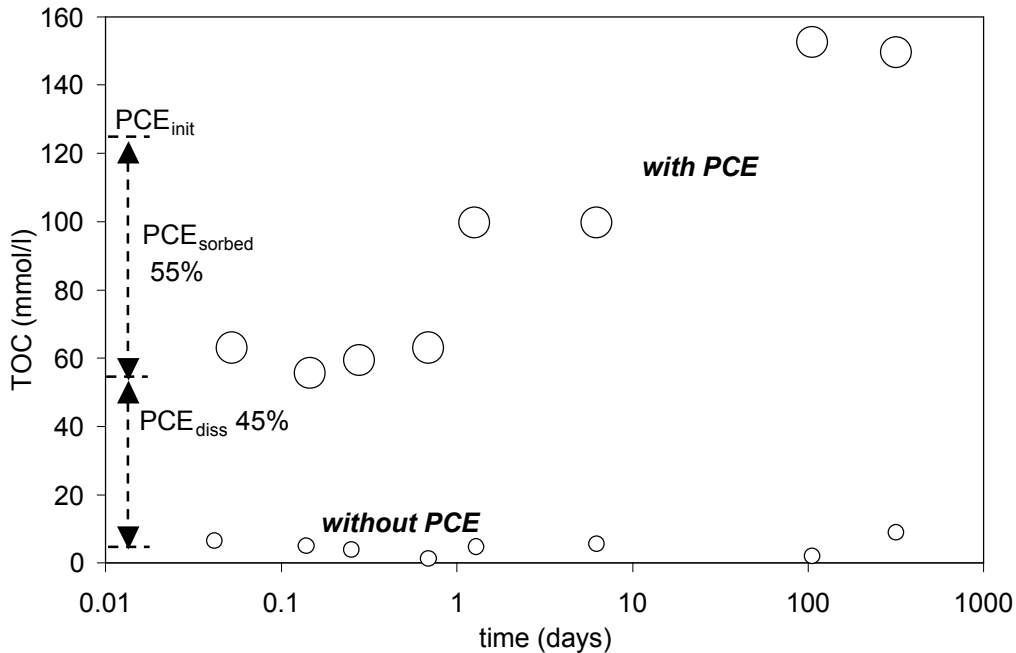


Fig. 5: Concentration of PCE (expressed as total organic carbon TOC) in the pore solution as a function of time.

3.4 Modelling

The modelling is based on the calculated hydration rates and thermodynamic calculations. The modelling results show in general a good agreement with the experimental data (Fig. 6A); only the predicted calcium and sulphate concentrations are 2 to 5 times lower than the measured concentrations. Initially, calcium, sulphate and hydroxide concentrations are limited by the presence of gypsum and portlandite. As ettringite precipitates anhydrite and gypsum are consumed resulting in a drastic decrease of calcium and sulphate concentrations and an increase in hydroxide concentrations after about 12 hours which agrees well with the experimental data (Fig. 6A).

Both, the composition of the pore solution in absence and in presence of PCE were modelled. In the case of OPC with PCE, for modelling the composition of PCE (i.e. TOC and Na_2SO_4) was considered. In addition, it was assumed that only 45% of PCE added (cf. Fig. 5) remained in the pore solution. The modelling predicted no differences between the composition of the pore solution in the absence and presence of PCE with exception of Na and TOC (cf. Fig. 6B). The calculations show that the observed increase of Na in the pore solution is due to the Na present in PCE (Fig. 6B). In addition, the good agreement between calculations and experimental observations indicates that in fact no significant complexation between PCE and dissolved ions such as Ca, Na, K, or Al takes place.

Similarly to the experimental data, the modelling predicts an increase of TOC in the pore solution with hydration as the amount of pore solution

decreases. After 6 and more days, the calculated TOC values are slightly higher than the measured values which could indicate a small further uptake of PCE or could also be due to the underestimation of the amount of pore solution in the calculations.

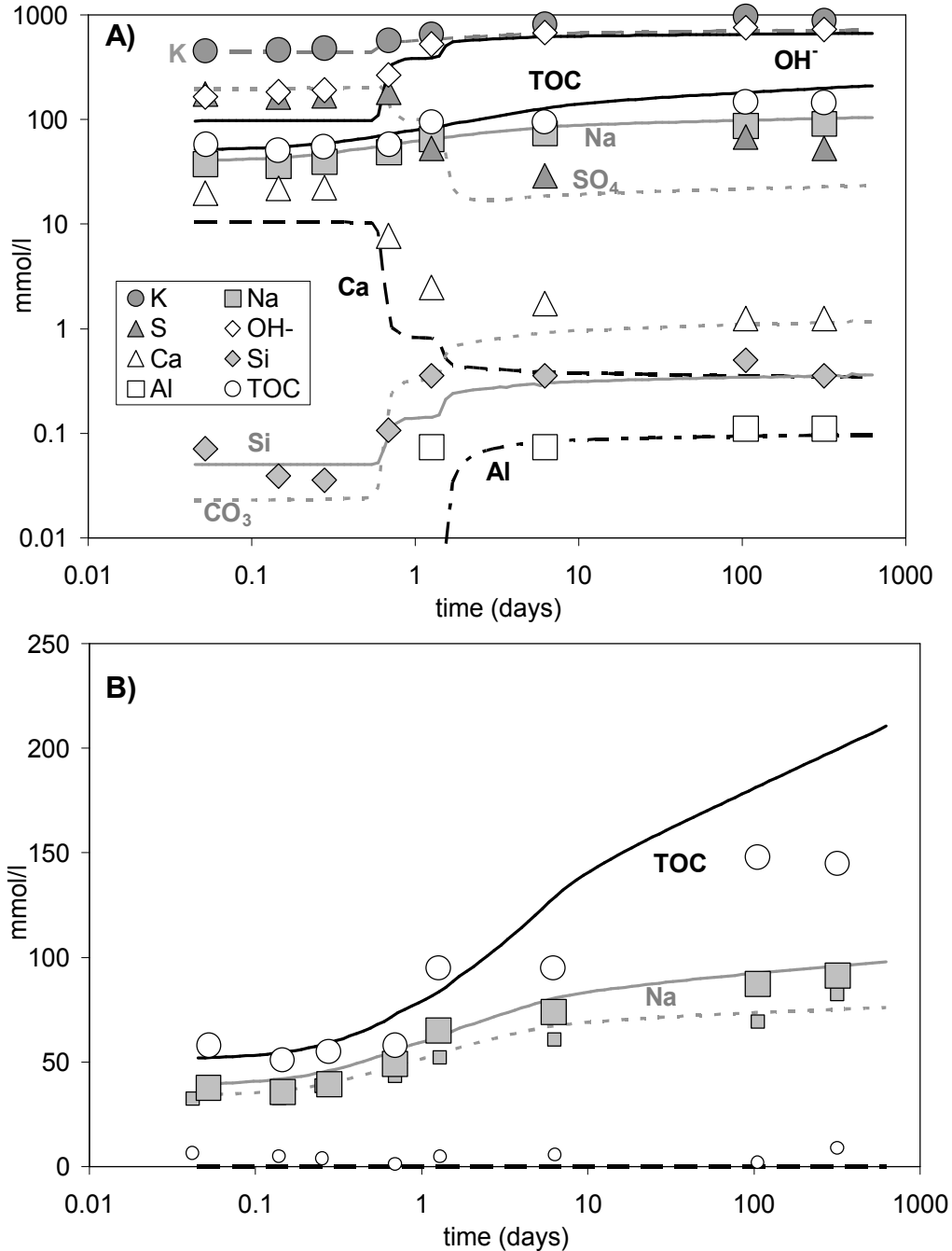


Fig. 6: A) Calculated (lines) and measured (points) concentrations in pore solution of OPC containing 0.4 wt-% PCE. B) Calculated (lines) and measured (large points) Na and TOC-concentrations in pore solution of OPC containing 0.4 wt-% PCE. Small points and dotted lines refer to OPC without PCE.

4 Conclusions

The investigation of the solid and liquid phase of hydrating Portland cement in the absence and presence of a polycarboxylate-based superplasticizer showed that the superplasticizer retarded during the first 30 hours the dissolution of alite strongly, thus delaying the formation of portlandite and C-S-H. Even though polycarboxylate-based superplasticizers adsorb strongly on aluminate, the retardation of the formation of ettringite was less distinct. In the presence of PCE after 6 hours of hydration no or very little ettringite has precipitated, after 16 hours the same amount of ettringite has formed as in the absence of PCE. At later times no significant difference in the amount of the different hydrates formed was observed.

Polycarboxylate-based superplasticizer do not affect the composition of the pore solution indicating that their retarding and plasticizing effect is not due to interaction with dissolved Ca^{2+} or other dissolved ions. This agrees with findings of Richter and Winkler [15] who reported low stability constants for complexes between Ca^{2+} and polyacrylic acid. Similarly, also for lignosulphonate-based SP no or only very weak complex formation between Ca^{2+} and lignosulphonate has been observed [19]. These findings confirm further that the effects of polycarboxylate-based superplasticizers concerning rheology and impact on hydration kinetics (retardation) are based rather on steric (and electrostatic) dispersion mechanisms [1] and on their sorption on solid phases present than on chemical interaction with the dissolved ions. About half of the polycarboxylate-based superplasticizer is taken up during the first hour by the solids present. After the first hour only a very limited further uptake was observed.

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References

- [1] H. Uchikawa, S. Hanehara, D. Sawaki, The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixture, *Cem Concr Res* 27 (1) (1997) 37-50
- [2] K. Yamada, T. Takahashi, S. Hanehara, M. Matsuhisa, Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer, *Cem Concr Res* 30 (2) (2000) 197-207
- [3] F. Winnefeld, S. Becker, J. Pakusch, T. Götz, Polymer structure / concrete property relations of HRWRA, in: 8th CANMET/ACI International Conference on Recent Advances in Concrete Technology, Montreal, May 31 - Jun 3, 2006, Suppl. Vol., pp. 159-177
- [4] F. Winnefeld, A. Zingg, L. Holzer, R. Figi, J. Pakusch, S. Becker, Interaction of polycarboxylate-based superplasticizers and cements:

influence of polymer structure and C₃A-content of cement, in: 12th ICCC, Montreal, July 8 -13, 2007

[5] R. J. Flatt, Y. Houst, A simplified view on chemical effects perturbing the action of superplasticizers, *Cem Concr Res* 31 (8) (2001) 1169-1176

[6] M. Y. A. Mollah, W. J. Adams, R. Schennach, D. L. Cocke, A review of cement-superplasticiser interactions and their models, *Adv Cem Res* 12 (4) (2000) 153-161

[7] W. Schwarz, Novel cement matrices by accelerated hydration of the ferrite phase in Portland cement via chemical activation: kinetics and cementitious properties, *Advn Cem Bas Mat* 2 (1995) 189-200

[8] D. Bonen, S. L. Sarkar, The superplasticizer adsorption capacity of cement pastes, pore solution composition, and parameters affecting flow loss, *Cem Concr Res* 25 (7) (1995) 1423-1434

[9] N. Mikanovic, M. A. Simard, C. Jolicoeur, Interaction between polynaphthalene sulfonate-type superplasticizers and cements during initial hydration, in: 6th CANMET/ACI international conference on superplasticizers and other admixtures in concrete, Nice, 2000, ACI Special Publication 195, pp. 561-584

[10] B. Lothenbach, F. Winnefeld, Thermodynamic modelling of the hydration of Portland cement, *Cem Concr Res* 36 (2) (2006) 209-226

[11] B. Lothenbach, E. Wieland, A thermodynamic approach to the hydration of sulphate-resisting Portland cement, *Waste Management* 26 (7) (2006) 706-719

[12] L. J. Parrot, D. C. Killoh, Prediction of cement hydration, *British Ceramic Proceedings* 35 (1984) 41-53

[13] F. Puertas, H. Santos, M. Palacios, S. Martínez-Ramírez, Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes, *Advn Cem Bas Mat* 17 (2) (2005) 77-89

[14] F. Puertas, T. Vázquez, Early hydration cement. Effect of admixtures superplasticizers, *Materiales de construcción* 51 (262) (2001) 53-61

[15] F. Richter, E. W. Winkler, Das Calciumbindevermögen, *Tenside Surfactants Detergents* 24 (4) (1987) 213-216

[16] K. Yoshioka, E. Tazawa, K. Kawai, T. Enohata, Adsorption characteristics of superplasticizers on cement component minerals, *Cem Concr Res* 32 (10) (2002) 1507-1513

[17] T. A. Bürge, Mode of action of superplasticizers, in: 6th CANMET/ACI international conference on superplasticizers and other admixtures in concrete, Nice, 2000, ACI Special Publication 195, pp. 101-125

[18] M. A. Glaus, A. Laube, L. R. Van Loon, Solid-liquid distribution of selected concrete admixtures in hardened cement pastes, *Waste Management* 26 (7) (2006) 741-751

[19] L. H. Grierson, J. C. Knight, R. Maharaj, The role of calcium ions and lignosulphonate plasticiser in the hydration of cement, *Cem Concr Res* 35 (2005) 631-636