The influence of the glass transition temperature (T_g) of polymers on early OPC hydration: a complete study of the heat flow, phase evolution, and pore solution chemistry

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Abstract The impact of two different dialyzed styrene-acrylate polymer dispersions on the early hydration of OPC was studied. The polymer particles of both dispersions show a similar particle size distribution and high charge due to carboxylic groups on the surface of the particles. Both dispersions also show similar adsorption behavior. The hydration of the OPC was studied at a polymer concentration below the initial adsorption in order to evaluate possible reasons for the interaction of the polymer particles with cement hydration. It can be shown that the polymer particle with the lower glass transition temperature T_g shows a stronger impact on cement hydration, which cannot be explained by any influence on the pore solution composition or the initial dissolution of cement phases. Hence, the adsorption mechanism seems to be the most likely cause of the interaction of the polymers with hydrating cement.

Keywords Cement hydration · Polymers · Pore solution · Retardation · Glass transition temperature

1 Introduction

Composite binders combining inorganic binders such as Ordinary Portland cement (OPC) as well as organic binders such as polymer dispersions are widely used in numerous applications. The additional use of such organic binders improves significant properties such as the flexural strength, water impermeability, or adhesive strength [1–3]. These properties are very important for applications such as tile adhesives, self-leveling underlayments, sealing slurries, or repair mortars for concrete.

It is well known that a range of compounds can retard cement hydration. This impact is not limited to only dispersed polymer particles but is also produced by water-soluble compounds and polymers. The most important retardation effect is certainly the retardation caused by superplasticizers, which has been studied in numerous publications (e.g. [4–7]). However, it has also been shown that water-soluble polymers that do not act as superplasticizers [8] as well as the aqueous phase of a dispersion containing e.g. water-soluble emulsifiers, protective colloids, or oligomers retard the cement hydration as well [9–11]. While the aqueous phase can lead to a pronounced prolongation of the induction period, the polymer particles can lead

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to a short prolongation of the induction period in addition to a significant slowdown of the hydration process during the main hydration [9].

Most polymer dispersions retard the hydration of OPC through a combination of both effects, retardation by the aqueous phase and retardation by the polymer particles. It has been shown that the negative charge density on the surface of the polymer particles is crucial for the retardation of OPC hydration. A higher charge results in a stronger retardation of the hydration process [12–14].

In literature, two possible interactions for the retardation of OPC hydration by polymer particles are discussed. The first possible interaction is the adsorption of polymer particles (also described in [15]) on cement or hydrate-phase grains, resulting in a steric hindrance of the hydrate-phase growth and/or the occupation of nucleation sites [16–19].

The second possible interaction is the complexation of calcium from the pore solution, leading to a decreased Ca concentration in a pore solution and as a result to slower hydrate-phase growth [20–23].

Recently, the glass transition temperature of polymer particles was discussed as another crucial factor for the effect on cement hydration. Lu et al. [24] and Han et al. [18] agree that soft polymers (with a very low T_g) have a stronger impact on the hydration of an OPC than harder polymers with a very high T_g . It is discussed in both publications that the deformation of polymer particles can lead to a higher surface coverage of the cement particles, producing a physical hindrance of the hydration process.

The intention of the present work is to expand the knowledge of the retardation of OPC hydration by polymer particles without any water-soluble compounds in the aqueous phase, especially with more data about the phase evolution, pore solution data, as well as data for saturation indices during hydration. This in turn can help to obtain an even more detailed view of the hydration of OPC with polymer particles.

2 Materials and methods

The temperature chosen for all experiments was 23 °C. The w/c ratio used for all experiments was 0.41. Deionized water was used for all experiments. Before the paste experiments described later in the manuscript were started, the cement was mixed

properly with water and/or dispersion. Mixing was done using a small electrical stirrer that allows the mixing of small sample amounts (2–4 g). The mixing speed applied was 860 rpm. The mixing produced a homogenous paste without bleeding or unwetted particles.

2.1 OPC used

The Ordinary Portland cement (OPC) used for this study was a commercial cement of the quality CEM I 52.5 R. A chemical analysis and phase content were obtained with X-ray fluorescence (XRF) and XRD measurements. The results of the XRF and XRD analysis are shown in Table 1.

2.2 Polymers used

Two different styrene acrylate copolymers with a varied monomer composition of *n*-butyl acrylate (BA) and styrene (St), as shown in Table 2, were synthesized by emulsion polymerization. Both polymers show a relatively similar particle size (DLS, Malvern Zetasizer 3000hs, UK) but different glass transition temperatures (T_g , measured by DSC Q2000, TA instruments®, USA) due to their different monomer composition. For one polymer that contains less BA than St, the T_g is higher than the one with more BA content. The polymer with a T_g of 58 °C was called hard polymer, while the polymer with a T_g of – 5 °C was called a soft polymer because of their different film-forming properties at room temperature (23 °C).

Table 1 Phase composition and chemical composition of the OPC used

Phase	wt%	Oxide	wt%
Alite	59	CaO	62.7
Belite	11	SiO ₂	20.1
C ₃ A _{cubic}	7	Al ₂ O ₃	5.5
Gypsum	3	Fe ₂ O ₃	3.3
Bassanite	2.4	MgO	2.8
Anhydrite	2.0	Na ₂ O	0.1
Calcite	4.4	K ₂ O	0.83
Syngenite	0.9	SO ₃	1.8
Brownmillerite	9	TiO ₂	0.2
		LOI	1.8

Table 2 Characteristics of the polymers used

Samples	Monomer composition (wt/%)		T_g	Surface charge	Particle diameter/nm	Charge density/(ueq/g)		pH
	St	BA				pH = 7	pH = 12	
Hard polymer	73	25	58 °C	–COO [–]	312	– 85	– 120	5.21
Soft polymer	36	62	– 5 °C	–COO [–]	271	– 85	– 162	5.18

During cement hydration, due to the continuous water consumption, the soft polymer is expected to form a polymer film, while the hard one would maintain a spherical form despite water consumption and evaporation. The other important characteristics of the polymer dispersions, such as the surface charge density (PCD 05, MÜtek Analytic, Herrsching, Germany), surface functional group, and pH, are also shown in Table 2.

Since the intention of this study is only to investigate the effect of the polymer particles on cement hydration, the dispersions were cleaned before the experiments were performed. The polymer dispersions were cleaned by dialysis in order to remove the components in the serum phase (oligomers, salts, residual monomers, emulsifiers). DI water as an eluent and a cellulose ester semipermeable membrane with a pore size of less than 10 nm were used. Dialysis was performed until the conductivity of the dialysate dropped from around 1000 $\mu\text{S}/\text{cm}$ to below 30 $\mu\text{S}/\text{cm}$. Dialysis per latex sample usually took at least 3 days.

2.3 Determination of the initial adsorption of the polymer particles

There is a scientific consensus that the adsorption of polymer particles occurs according to a specific pattern. Firstly, an almost complete adsorption can be detected up to a certain amount of polymer in relation to cement. At higher dosages, polymer particles are spread on the surface of the cement grains as well as in the pore solution of the cement [9, 15, 25].

The adsorption of the above-mentioned polymer latexes was also studied in cement pastes. Cement paste was prepared by thoroughly mixing 50.0 g cement with DI water and a varied amount of polymer latex for 1 min using a hand mixer. The w/c of the cement paste was fixed at 0.41, and the water amount

introduced by the addition of the latex was taken into account. The well-mixed fresh cement paste was then introduced into a centrifuge tube and centrifuged at 4000 rpm for 5 min. The supernatant liquid was collected using a syringe. The solid content of the supernatant liquid was measured by completely drying the liquid in an evacuated oven at 100 °C for 2 h. It is known that the obtained solid contains salts from the interstitial solution of fresh cement paste and residual polymer in the aqueous phase. Usually the solid content of the supernatant liquid of the blank cement paste is in a range of 2.1–2.3% and originates from the various salts and alkalis in the interstitial solution of fresh cement paste. As seen in Fig. 1, the mass loss of such solid occurs mainly in the temperature ranges of 400–550 °C, which is believed to be caused by the existence of dissolved $\text{Ca}(\text{OH})_2$ in the pore solution. This part of the mass loss is around 9% and the residue is around 91%. For the pure polymers, one can see that the major mass loss takes place in the temperature range of 320–400 °C and the residual content of the sintered polymer after 600 °C is around 1.7% for the soft polymer and 0.9% for the hard polymer. Therefore, we ignored this part in our study, and we assume that the polymers are totally burned during the sintering process of 100–600 °C. For a unit gram of the dried supernatant liquid of the cement pastes containing a varied amount of polymers, the mass loss (M_{loss}) mainly occurs in the temperature range of 320–450 °C and is caused both by the polymer and the decomposition of $\text{Ca}(\text{OH})_2$. The residue after 600 °C sintering (denoted as M_{res}) contains mostly the sintered salts from the pore solution. In Fig. 1, the polymer content in the dried solid part of the supernatant liquid could be calculated as $M_{\text{loss}} - M_{\text{res}} \times 0.09/0.91$. In order to quantify the polymer content in the supernatant liquid [polymer (%)], a certain amount of the supernatant liquid (M_{liquid}) was dried at 100 °C to achieve a constant weight (approx. 2 h). The dried solid (M_{solid}) was sintered at 600 °C for 1 h in a

Fig. 1 TGA curves of the dried pure polymer latexes (hard polymer and soft polymer) and the dried supernatant liquid (pore solution = PS) of various cement pastes (blank, hard polymer 15% and soft polymer 15%)

ceramic container, and the mass loss (M_{loss}) as well as the residue amount (M_{res}) was measured. The polymer content in the supernatant liquid was then calculated from the equation below:

$$\text{Polymer (\%)} = \frac{(M_{\text{loss}} - M_{\text{res}} \times 0.09/0.91)}{(M_{\text{liquid}})} \times 100$$

In this way, the concentration of polymer remaining in the aqueous phase was quantitatively determined. The amount of the adsorbed polymer can be calculated by subtracting the amount of polymer remaining in the aqueous solution from the amount of polymer initially added to the cement paste.

2.4 Heat flow calorimetry

Heat flow calorimetry was performed using a TAM Air calorimeter from TA Instruments. Before measuring, the samples were equilibrated at 23 °C. Samples were carefully mixed externally with a spatula for 1 min. Between 1 and 2 g of paste were filled in the ampoules for measurement. The curves obtained were normalized with respect to the amount of cement used (mW/g).

2.5 In-situ XRD

In-situ XRD was applied in order to follow the phase composition of the samples quantitatively. XRD has the advantage that the crystalline phases during OPC hydration can be quantified by their characteristic peaks, which occur as a function of the space between the lattice plains in a crystal. The dry cement was mixed with water and/or dispersion and then placed into a special sample holder that allowed temperature control during measurement [10, 26, 27]. XRD patterns were recorded in situ, hence it was not necessary to stop the hydration process. The time needed for each pattern was 0.25 h. Before measuring, the samples were covered with Kapton film in order to avoid carbonation and evaporation of water. Rietveld refinement (applying the Bruker software Topas) was used in order to interpret the measured intensities quantitatively. Rietveld refinement only considers the crystalline part of the sample, which makes it necessary to combine it with an external standard method [28–30] in case that non-crystalline phases (e.g. missing water) are in the sample. The values from the combination of both methods result in absolute values of wt% in the cement paste. These values are plotted in the following figures in the manuscript. The

crystal structures used for the Rietveld refinement are shown in Table 3.

2.6 Pore solution analysis

Pore solution analysis was performed in order to obtain information about the dissolved ions and the saturation indices of the possible phases. In earlier times, pore solution was extracted by centrifugation, and later on a solution was extracted by pressing. Afterwards, the ionic concentrations were measured applying quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS). Due to the complex matrix and the low amount of silicon in the pore solution, silicon was measured using the standard addition method.

Before measuring, the pore solution was filtered through a 200 nm filter in order to remove any cement particles. Additionally, the pore solution was acidified using HNO_3 in order to avoid the crystallization of hydrate phases during storage before measurement.

The software PHREEQC [43] was applied in order to calculate species distribution in the pore solution as well as the saturation indices of the phases of interest. Since the ionic strength of the pore solution is around 0.3 M, the Pitzer approach was applied in order to account for the ion-ion interaction. The database used, including the solubility products for C–S–H and ettringite, is consistent with the database of Blanc et al. [44, 45]. The C–S–H solubility product with a C/S ratio of 1.6 was used for the calculation of the saturation indices for C–S–H at different point in time during hydration.

When using pore solution extraction with pressure, one must always take into account that some drawbacks are possible. On the one hand, it is possible that some crystalline phases might be destroyed by the applied pressure, and on the other hand, it is also possible that the extracted pore solution does not represent the high ionic charge near the surface of the cement particles. However, the extraction of pore solution by either centrifugation or pressing is still state of the art inasmuch as no other methods are available at present.

3 Results

Figure 2 shows the initial adsorption of the polymers used in this study on the cement used. It can be seen that there is a complete adsorption of the polymer particles until around 10% with regard to the amount of cement used. In the present study, an amount of 10% was chosen for the experiments. This amount leads to a clean pore solution in which no polymer can be detected. This pore solution in turn can be measured directly without any additional treatment (e.g. removing polymer particles from pore solution).

Hence, the present study concentrates on the surface effects of the adsorbed polymer particles, but not on a possible interaction of the free polymer particles with the ions dissolved in the pore solution.

Figure 3 shows the impact of 10 wt% of the polymers used on the hydration of the OPC used. It can be seen that both polymers influence the heat flow. The hard polymer has less impact than the soft polymer. Both polymers show a short prolongation of the induction period. The acceleration period starts later when polymers are present. The soft polymer leads to a more prolonged induction period than the hard polymer. There is also a big impact on the maximum heat flow during the main period of hydration when the polymer particles are present. The maximum heat flow recorded during the main period is around 3.5 mW/g for the blank paste, and it decreases when the polymers are added. The main heat during the main period is around 2.8 mW/g for the hard polymer and around 2 mW/g for the soft polymer. The duration of the main period is also prolonged when polymer particles are added. The duration for the blank system is around 20 h. While the duration of the main period with the hard polymer

Table 3 Structures used for Rietveld refinement

Structure	Literature
Alite	[31]
Belite	[32]
$\text{C}_3\text{A}_{\text{cubic}}$	[33]
Gypsum	[34]
Bassanite	[35]
Anhydrite	[36]
Calcite	[37]
Syngenite	[38]
Portlandite	[39]
Ettringite	[40]
C–S–H	[41]
Brownmillerite	[42]

Fig. 2 Initial adsorption of the polymers used

Fig. 3 Heat flow curves (error ± 0.1 mW/g) of the cement when used with and without polymer particles

seems to be almost comparable to the blank system, the duration of the main period is around 35 h when the soft polymer is added.

Figure 4 shows the results from in situ XRD. The quantitative development of the alite phase as well as the reaction turnover of the alite phase is plotted. It can be seen that both polymers slow down the reaction turnover of the main alite phase. The hard polymer shows a significantly lower impact on the hydration

than the soft polymer. After 24 h alite reaches only two-thirds of the reaction turnover with the soft polymer when compared to the blank system.

The influence of the polymer particles on the ettringite formation is shown in Fig. 5. It can be seen that both polymers show a significant impact on the formation of ettringite. Both polymers lead to a significantly lower amount of ettringite formed after 24 h.

In addition to the presented examination methods, pore solution analysis was performed in order to see if the adsorbed polymers have an impact on the pore solution chemistry, which may be caused by hindering the dissolution of the cement phases.

For the blank cement, the pore solution composition evolves as shown in Fig. 6 [see also 26]. At the beginning, a Ca concentration of around 1000 mg/l can be detected. The silicon concentration is much lower at around 1–2 mg/l. After several hours (here 7 h), the long-range ordered C–S–H phase can be detected, and the pore solution composition changes. While the calcium concentration decreases, the silicon concentration increases. Figure 6 also shows the calculated saturation index for C–S–H. It can be seen that at early stages there is a high oversaturation for C–S–H, which decreases over time until the pore solution

Fig. 4 Alite quantities (error ± 1 wt%) and reaction turnover of alite with and without the addition of polymers

Fig. 5 Ettringite formation (error ± 1 wt%) during hydration of the OPC used with and without polymer addition

is almost in equilibrium with C–S–H but still oversaturated.

Figure 7 shows the sulfur and aluminum concentration in the pore solution, the saturation index of ettringite, and the phase evolution for C_3A , gypsum and ettringite. It can be seen that there is a very high sulfur concentration in the pore solution, while the

aluminum concentration is very low. After the last sulfate carrier, gypsum, is dissolved after around 12 h, a massive drop in the sulfur content in the pore solution can be detected. After the sulfur concentration drops, an increase in the aluminum concentration can be seen. This increase is certainly triggered by the ongoing dissolution of C_3A , which was blocked by sulfate at early hydration times [26]. The oversaturation of ettringite is very high at the very beginning of hydration but drops significantly after several hours. At later points in time, the saturation index of ettringite turns to negative values, which is due to the completed sulfate consumption from the pore solution.

Figure 8 shows the heat flow curves of the examined systems as well as the calcium and silicon concentrations of the examined systems. It can be seen that the evolution of the pore solution is comparable but with a time shift when polymers are added. It can also be seen that calcium starts in all systems at a very high concentration that is comparable to the concentration in the blank system. The silicon concentration is much lower but also comparable in the three examined systems. The development/shift of the pore solution (decrease in calcium concentration, increase in silicon concentration) is comparable to the blank

Fig. 6 Alite and C-S-H quantities (error ± 4 wt%), Ca and Si concentrations and the saturation index of C-S-H during hydration of the used OPC

Fig. 7 C₃A, gypsum and ettringite quantities, S and Al concentrations, and the saturation index of ettringite during hydration of the used OPC

system in the presence of polymers but occurs at later points in time. As shown in Fig. 6, the shift in the pore solution composition takes place at the point in time where long-range ordered C-S-H is formed. Hence, it is possible that the shift of the pore solution composition is retarded because the polymers lead to a

significantly later formation of the long-range ordered C-S-H as shown indirectly for the alite turnover in Fig. 3 and directly in Fig. 9 for the blank system and the systems with polymer added.

Figure 10 shows the heat flow curves of the examined systems as well as the saturation indices

Fig. 8 Heat flow curves and Ca, Si concentrations in the pore solution with and without polymers

Fig. 9 C-S-H formation (error ± 4 wt%) quantified by XRD during hydration of the OPC used without polymer and with addition of the soft polymer

for C-S-H as calculated. It can be seen that the saturation indices are absolutely comparable at the beginning of hydration. Since the C-S-H phase is formed later in the systems with polymer, the shift in the pore solution composition occurs later and the oversaturation with respect to C-S-H stays constant at a higher level for a longer time period if polymers are present. However, the formation of C-S-H is significantly retarded in the presence of polymers. Hence, it

seems that the lower formation rate of C-S-H cannot be explained by the chemical force resulting from the pore solution composition.

The same can be seen for the formation of the ettringite phase as shown in Fig. 11. Both polymers show a significant impact on the formation of ettringite. Even at later points in time, at around 15 h, when the saturation index for ettringite is much lower in the blank system than in the systems with polymers, a significantly slower precipitation of ettringite can be detected.

4 Discussion and conclusion

Figure 12 summarizes the potential mechanisms affecting the hydration of an OPC if polymer particles are present. The interaction of the non-adsorbed polymer particles is not discussed here, because only concentrations were studied that are below the initial adsorption of the polymer particles. However, detailed data concerning phase development and pore solution is presented for the first time using cleaned polymer dispersions. In this way, the impact of polymer particles on cement hydration without the influence of the aqueous phase can be discussed. The adsorption of polymer particles on a cement surface seems to be a

Fig. 10 Saturation indices for C–S–H and heat flow curves during hydration of the OPC used with and without polymer addition

Fig. 11 Saturation indices for ettringite and ettringite quantities during hydration of the OPC used with and without polymer addition

crucial factor. This is discussed in the introduction to this paper and is well known for polymers that act as water reducers and superplasticizers [46].

Potential mechanism 1, assuming that adsorbed polymer particles can hinder the dissolution of the cement phases, was recently discussed [6] for water-soluble superplasticizers but seems to be negligible in our system with polymer particles when considering

the results from the presented study. It can be seen that the pore solution compositions do not vary at the beginning of hydration and during the induction period in the presence of the examined amount of polymer particles, resulting in comparable saturation indices for C–S–H and ettringite in all examined systems. A hindrance of the dissolution of a clinker phase such as alite or C_3A would lead to a lower

Fig. 12 Potential interactions of polymer particles with OPC

concentration of ions in the pore solution and as a consequence to a lower oversaturation. Additionally, it can be seen that the saturation index for ettringite stays comparably high for a long hydration time in the system with the soft polymer but the ettringite formation rate is the lowest of the all systems examined.

Mechanisms 2 and 3 are more likely (steric hindrance of the growth of hydrate phases (as discussed in [16–19]) and/or the occupation of nucleation sites), because it could be detected that although the oversaturation is comparably high, the formation and growth of C–S–H and ettringite are retarded. From data presented for C–S–H it cannot be distinguished if the added polymers occupy the nucleation sites for the hydrate phases formed or if the adsorbed polymer particles directly hinder the growth of the hydrate phases.

Considering the results for ettringite, the mechanism of growth hindrance seems most likely. Ettringite can be detected at the beginning of hydration in all systems, hence it can be assumed that the nucleation of ettringite is possible in the examined systems with and without polymers added. While the oversaturation with respect to ettringite is comparable to the blank system when polymers are added, a significantly lower

amount and slower formation rate can be detected, leading to the conclusion that the formation of ettringite seems to be hindered by steric issues.

Based on the data presented, the following conclusions can be drawn. The hydration of OPC was examined in blank paste and with the addition of polymer particles. A polymer dosage below the detectable adsorption was chosen so that the pore solution was almost free of polymer particles. No statements can be made concerning the potential complexation of ions by the non-adsorbed polymer particles in the pore solution. The impact of polymer particles with the chosen amount is most likely caused by surface effects on the cement or hydrate phase grains where the polymers are adsorbed [as also discussed in 16, 17], perhaps hindering the nucleation but certainly the growth of the hydrate phases. A soft polymer shows a higher impact on hydration in comparison to a hard polymer, which indicates that with a comparable adsorbed amount of polymer, the soft polymer covers a larger area of cement grains or hydrates due to the deformability of the polymer particles. This seems to be in line with the findings from other research groups [18] and prework of the authors [24].

5 Conclusion

- The impact of the adsorbed polymer on the dissolution of clinker phases is less likely to be the cause for the retardation of polymers on cement hydration, in view of the initial concentration of Ca and Si as well as the saturation indices of CSH and Aft.
- Soft polymer exhibits stronger retardation of cement hydration than hard polymer. The formation of both CSH and AFT is severely slowed down by the soft polymer.
- Surface effects of the polymer on the cement or hydrate phase grains is more likely for retardation. The adsorbed polymer may hinder the nucleation and growth of the hydration products by occupying the effective sites. The soft polymer showing a stronger impact on hydration than the hard polymer suggests that at a certain polymer adsorption, the soft polymer covers a larger area of cement grains or hydrates due to the deformability of the polymer particles. This is in line with the findings from other research groups.

Compliance with ethical standards

Conflict of interest The authors wish to confirm that there are no known conflicts of interest associated with this publication.

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References

- Ohama Y (1998) Polymer-based admixture. *Cem Concr Compos* 20:189–212
- Sakai E, Sugita J (1995) Composite mechanism of polymer modified cement. *Cem Concr Res* 25:127–135
- De Vekey RC, Majumdar AJ (1975) Durability of cement pastes modified by polymer dispersions. *Mater Struct* 8:315–321
- Winnefeld F, Becker S, Pakusch J, Götz Th (2007) Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems. *Cem Concr Compos* 29:251–262
- Zhang Y-R, Kong X-M, Lu Z, Lu Z-B, Hou S-S (2015) Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes. *Cem Concr Res* 67:184–196
- Marchon D, Juilland P, Gallucci E, Frunz L, Flatt RJ (2017) Molecular and submolecular scale effect of comb-copolymers on tri-calcium silicate reactivity: towards molecular design. *J Am Ceram Soc* 100:8171–8841
- Sowoidnich Th, Rachowski T, Rößler Ch, Völkel A, Ludwig H-M (2015) Calcium complexation and cluster formation as principal modes of action of polymers used as superplasticizer in cement systems. *Cem Concr Res* 73:42–50
- Jansen D, Goetz-Neunhoffer F, Neubauer J, Haerzschel R, Hergeth W-D (2013) Effect of polymers on cement hydration: a case study using substituted PDADMA. *Cem Concr Compos* 35:71–77
- Kong X-M, Emmerling S, Pakusch J, Rueckel M, Nieberle J (2015) Retardation effect of styrene-acrylate copolymer latexes on cement hydration. *Cem Concr Res* 75:23–41
- Jansen D, Goetz-Neunhoffer F, Neubauer J, Hergeth WD, Haerzschel R (2010) Influence of polyvinyl alcohol on phase development during the hydration of Portland cement. *ZKG Int* 63:100–107
- Jin Y, Stephan D (2018) Hydration kinetics of Portland cement in the presence of vinyl acetate ethylene latex stabilized with polyvinyl alcohol. *J Mater Sci* 53:7417–7430
- Lu Z, Kong X-M, Zhang Ch, Jansen D, Neubauer J, Goetz-Neunhoffer F (2019) Effects of two oppositely charged colloidal polymers on cement hydration. *Cem Concr Compos* 96:66–76
- Dimmig-Osburg A, Pietsch I, Pakusch J (2006) Polymer additives and their influence on the cement microstructure in the early stages of hardening. *ZKG Int* 5:72–83
- Kong X, Pakusch J, Jansen D, Emmerling S, Neubauer J, Goetz-Neunhoffer F (2016) Effect of polymer latexes with cleaned serum on the phase development of hydrating cement pastes. *Cem Concr Res* 84:30–40
- Plank J, Gretz M (2008) Study on the interaction between anionic and cationic latex particles and—Portland cement. *Colloids Surf A Physiochem Eng Asp* 330:227–233
- Silva DA, Monteiro PJM (2005) ESEM analysis of polymeric film in EVA-modified cement paste. *Cem Concr Res* 35:2047–2050
- Silva DA, Monteiro PJM (2005) Hydration evolution of C₃S-EVA composites analysed by soft X-ray microscopy. *Cem Concr Res* 35:351–357
- Han D, Chen W, Zhong S (2017) Physical retardation mechanism of latex polymer on the early hydration of cement. *Adv Cem Res* 30:113–122
- Su Z, Sujata K, Bijen MJM, Jennings HM, Fraaij ALA (1996) The evolution of the microstructure in styrene acrylate cement-modified cement pastes at the early stage of cement hydration. *Adv Cem Based Mater* 3:87–93

20. Larbi JA, Bijen J (1990) Interaction of polymers with Portland cement during hydration: a study of the chemistry of the pore solution of polymer modified cement systems. *Cem Concr Res* 20:139–147
21. Betioli AM, Hoppe Filho J, Cincotto MA, Gleize PJP, Pileggi RG (2009) Chemical interaction between EVA and Portland cement hydration at early-age. *Constr Build Mater* 23(11):3332–3336
22. Baueregger S, Perello M, Plank J (2015) Impact of carboxylated styrene-butadiene copolymer on the hydration kinetics of OPC and OPC/CAC/AH: the effect of Ca^{2+} sequestration from pore solution. *Cem Concr Res* 73:184–189
23. Qu C, Zhao X (2017) Influence of SBR latex and HPMC on the cement hydration at early age. *Case Stud Constr Mater* 6:213–218
24. Lu Z, Kong X-M, Zhang Ch, Cai Y, Zhang Q, Zhang Y (2017) Effect of polymer latexes with varied glass transition temperature on cement hydration. *J Appl Polym Sci* 134(36):45264
25. Lu Z, Kong X-M, Zhang Ch, Cai Y (2018) Effect of highly carboxylated colloidal polymers on cement hydration and interactions with calcium ions. *Cem Concr Res* 113:140–153
26. Jansen D, Naber C, Ectors D, Lu Z, Kong X-M, Goetz-Neunhoeffler F, Neubauer J (2018) The early hydration of OPC investigated by in situ XRD, heat flow calorimetry, pore water analysis and ^1H -NMR: learning about adsorbed ions from a complete mass balance approach. *Cem Concr Res* 109:230–242
27. Wolf JJ, Jansen D, Goetz-Neunhoeffler F, Neubauer J (2019) Mechanisms of early ettringite formation in ternary CSA-OPC-anhydrite systems. *Adv Cem Res*. <https://doi.org/10.1680/jadcr.18.00115>
28. O'Connor BH, Raven MD (1988) Application of the rietveld refinement procedure in assaying powdered mixtures. *Powder Diffr* 3:2–6
29. Jansen D, Stabler Ch, Goetz-Neunhoeffler F, Dittrich S, Neubauer J (2011) Does Ordinary Portland (OPC) contain amorphous phase? A quantitative study using an external standard method. *Powder Diffr J* 26:31–38
30. Schreiner J, Jansen D, Ectors D, Goetz-Neunhoeffler F, Neubauer J, Volkmann S (2018) New analytical possibilities for monitoring the phase development during the production of autoclaved aerated concrete. *Cem Concr Res* 107:247–252
31. De La Torre AG, Bruque S, Campo J, Aranda MAG (2002) The superstructure of C_3S from synchrotron and neutron powder diffraction and its role in quantitative phase analysis. *Cem Concr Res* 32:1347–1356
32. Jost KH, Ziemer B, Seydel R (1977) Redetermination of the structure of β -dicalcium silicate. *Acta Crystallogr Sect B: Struct Crystallogr Cryst Chem* 33:1696–1700
33. Mondal P, Jeffery J (1975) The crystal structure of tricalcium aluminate, $\text{Ca}_3\text{Al}_2\text{O}_6$. *Acta Crystallogr Sect B: Struct Crystallogr Cryst Chem* 31:689–697
34. Pedersen BF (1982) Neutron diffraction refinement of the structure of gypsum. *Acta Crystallogr Sect B: Struct Crystallogr Cryst Chem* 38:1074–1077
35. Weiss H, Bräu MF (2009) How much water does calcined gypsum contain? *Angew Chem Int Ed* 48:3520–3524
36. Kirfel A, Will G (1980) Charge density in anhydrite CaSO_4 , from X-ray and neutron diffraction measurements. *Acta Crystallogr Sect B: Struct Crystallogr Cryst Chem* 36:288–2890
37. Maslen EN, Streltsov VA, Streltsova NR (1995) Electron density and optical anisotropy in rhombohedral carbonates. III. Synchrotron X-ray studies of CaCO_3 , MgCO_3 and MnCO_3 . *Acta Crystallogr Sect B: Struct Sci* 51:929–939
38. Bokii GB, Palchick NA, Antipin MYu (1978) More precise determination of syngenite crystal structure. *Kristallografiya* 23:257–260
39. Busing WR, Levy HA (1986) Neutron diffraction study of calcium hydroxide. *Acta Crystallogr Sect B: Struct Sci* 42:51–55
40. Renaudin G, Filinchuk Y, Neubauer J, Goetz-Neunhoeffler F (2010) A comparative structural study of wet and dried ettringite. *Cem Concr Res* 40:370–375
41. Bergold ST, Goetz-Neunhoeffler F, Neubauer J (2013) Quantitative analysis of C–S–H in hydrating alite pastes by in situ XRD. *Cem Concr Res* 53:119–126
42. Jupe AC, Cockcroft JK, Barnes P, Colston SL, Sankar G, Hall C (2001) The site occupancy of Mg in the brownmillerite structure and its effects on hydration properties: an X-ray/neutron diffraction and EXAFS study. *J Appl Crystallogr* 34:55–61
43. Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (version 2)—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Water Resour Investig Rep* 99–4259:312
44. Blanc Ph, Bourbon X, Lassin A, Gaucher EC (2010) Chemical model for cement-based materials: temperature dependence of thermodynamic functions for nanocrystalline and crystalline C–S–H phases. *Cem Concr Res* 40:851–866
45. Blanc Ph, Bourbon X, Lassin A, Gaucher EC (2010) Chemical model for cement-based materials: thermodynamic data assessment for phases other than C–S–H. *Cem Concr Res* 40:1360–1374
46. Gelardi G, Flatt RJ (2016) Working mechanisms of water reducers and superplasticizers, science and technology of concrete admixtures. Woodhead Publishing, Sawston, pp 257–278

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