



Interaction of Superplasticizers with Cement from the Point of View of Colloid Chemistry

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Abstract. When cement is mixed with water, the clinker phases immediately start to dissolve and a large amount of ions is released into the pore solution. As a result, the ion concentration rapidly increases until the aqueous phase is supersaturated, at which first hydration products are precipitated. As the dissolution, crystallization and the initial hydration reactions all occur at the solid-liquid interface, it is appropriate to consider early cement hydration from the aspects of colloid and interface science.

Generally, fresh cement pastes constitute a thermodynamically unstable colloidal dispersion of mesoscopic particles and hydrate phases in water. The rheological properties (e.g. viscosity, yield stress) and the stability are affected by colloidal and interparticle interactions (e.g. Brownian effects, hydrodynamic and contact forces). However, the poor workability of cement suspensions can be attributed to attractive van der Waals forces between cationic and anionic surface areas. To overcome those forces, superplasticizers are added which disperse cement by imparting an electrostatic (polycondensates) or steric (polycarboxylates) effect. Superplasticizers can interact with cement via adsorption (=physisorption), chemisorption (=intercalation into early hydrate phases) or at low water-to-cement ratios even through repulsive depletion forces induced by the portion of non-adsorbed polymers remaining in the pore solution.

In light of this, the aim of the paper is to give an overview of the different kinds of interactions of superplasticizers with cement from a colloid chemistry point of view. It will be shown, to which thermodynamic parameters the adsorption process is subjected and how the chemical composition of the polymers affects the adsorption behavior. Additionally, experimental methods will be presented that are commonly applied for the investigation of cement-superplasticizer interactions (adsorption and zeta potential measurements). Finally, the role of non-adsorbed superplasticizer molecules on the dispersion of cementitious systems with high solid volume fractions will be discussed.

Keywords: Dispersion · Adsorption · Superplasticizer · Colloid chemistry · Adsorbed layer thickness

1 Dispersion Mechanism of Superplasticizers

Ordinary Portland cement comprises silicate (C_3S , C_2S) and aluminate phases (C_3A , C_4AF) as well as sulfate carriers (e.g. gypsum) for the regulation of the set behavior. When suspended in water, the clinker phases develop a heterogeneous surface charge which leads to the flocculation of the cement particles [1]. Thus, some of the mixing water is entrapped resulting in a high viscosity. However, the agglomerates can be dissipated by the addition of superplasticizers like polycondensates or polycarboxylates (PCEs) which modify the interparticle forces.

It is well established that polycondensates disperse cement through an electrostatic effect, while PCEs achieve dispersion through a combination of electrostatic and steric repulsive forces [2, 3]. To achieve dispersion the superplasticizers need to adsorb at the solid-liquid interface. After adsorption the particles exhibit a negative surface charge which provokes an electrostatic repulsion whose magnitude is much stronger for polycondensates due to their higher anionicity. The electrostatic stabilization of colloidal suspensions is described by the DLVO theory developed by Derjaguin, Landau, Verwey and Overbeek. According to this model, the dimension of the electrostatic effect depends on the electric charge and the Debye length that represents the thickness of the ion cloud surrounding the suspended particles. In contrast to polycondensates, PCEs additionally impart a steric effect induced by their polyethylene glycol side chains [2]. These non-ionic lateral chains protrude into the pore solution and prevent cement particles from approaching each other too close. The steric effect correlates with the thickness of the adsorbed polymer layer, as obvious from the Ottewill-Walker equation:

$$V_{\text{steric}}(a) = \frac{4\pi kTC_v^2}{3v_1^2\rho_2^2}(\psi_1 - \kappa_1)(\delta - a)^2\left(3R + 2\delta + \frac{a}{2}\right)$$

where C_v is the concentration of the adsorbed polymer, v_1 is the molecular volume of the solvent molecules, δ is the adsorbed layer thickness, ρ_2 is the density of the adsorbate (polymer), ψ_1 is the entropy, κ_1 is the enthalpy, R is the radius of the adsorbate, and a is the distance between two adsorbate particles.

The importance of the adsorbed layer thickness for the steric stabilization is supported by findings from Houst et al. who showed that PCEs with longer side chains are more powerful dispersants than those exhibiting shorter ones [4]. Therefore, knowing the layer thickness can help to better understand the differences in the performance characteristics of superplasticizers. Unfortunately, the experimental determination is not very easy because no direct measurement on cement particles is possible due to the continuous changes of their surface composition during the hydration reactions. So far, the layer thicknesses of only a limited number of PCE products have been assessed, most often by atomic force microscopy (AFM) using non-reactive substrates like quartz, mica or magnesium oxide (MgO) [5]. This method produced relatively low values for the layer thickness (1 nm–4 nm) which are far below the values calculated for ideally stretched side chains. For example, many common PCEs exhibit lateral side chains made up of 45 ethylene oxide units which in an ideally stretched conformation

would spread over ~ 12.5 nm. The low values for the layer thickness are often ascribed to compression of the polymer layer by the negatively charged AFM tip. Based on those results, it is argued that AFM is an appropriate method to determine the actual adsorbed layer thickness of PCEs. Thus, more reliable information from additional methods is required to obtain a better understanding of the actual dimensions of the adsorbed layer thickness.

Recently, molecular dynamics simulations (MDS) were carried out to investigate the adsorption behavior of PCEs (MPEG-, APEG- and IPEG-PCE) on MgO in synthetic cement pore solution [6]. It was found that the adsorbed conformation is sensitive to the initial orientation of the polymers against the MgO surface. To be more specific, a parallel orientation favored a train like conformation, whereas a perpendicular one was more beneficial for a loop or tail shaped adsorption mode. Depending on the chemical composition of the PCEs quite different conformations were obtained (Fig. 1). According to the results of the MD simulations, the MPEG-PCE adsorbs in a rather flat conformation (=train) covering a large surface area that results in a thin layer thickness. However, the APEG-PCE provokes a medium but dense polymer layer. The highest layer thickness was observed for the IPEG-PCE that adsorbs in a tail like conformation mode. By interconnecting these findings with results from adsorption and fluidity tests it was inferred that a layer thickness higher than 6 nm is necessary for a high dispersing efficacy at a standard dosage of the PCE [6].

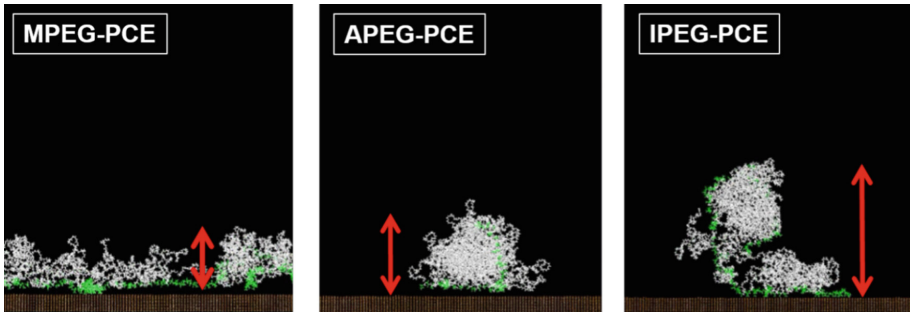


Fig. 1. Adsorbed conformations of different PCEs on MgO as obtained by MD simulations.

2 Adsorption Behavior of Superplasticizers

The working mechanism of superplasticizers relies on physical adsorption (=physisorption) of the anionic polymers on oppositely charged surface areas. Generally, adsorption is a dynamic process with three fundamental steps including the diffusion of the polymers to the solid-liquid interface, the physical attachment to the surface and the final rearrangement of the polymer layer until a maximum number of binding points is achieved [7]. From an energetic perspective, adsorption spontaneously occurs when the Gibbs free energy of adsorption ΔG is negative in sign. According to the Gibbs Helmholtz equation ($\Delta G = \Delta H - T \cdot \Delta S$) this is the case, when heat is released ($\Delta H < 0$) and/or the entropy of the system increases ($\Delta S > 0$). However, depending on

the molecular composition of the superplasticizer, enthalpy or entropy may be the prevalent parameter which instigates adsorption [8]. The experimental determination of ΔH and ΔS for polycondensates revealed that their adsorption is mainly driven by enthalpic contributions resulting from strong electrostatic interactions of the highly anionic polymers with the particle surface. For PCEs, adsorption primarily derives from a huge gain in entropy owed to the release of a large amount of ions and water molecules from the particle surface and the hydrate shell of the polymer [8].

The adsorption behavior of superplasticizers can be modified by the molecular weight, chemical composition and the overall polymer structure. It is well known, that differences in the adsorption properties entail quite diverging performance characteristics (e.g. slump retention capability). For instance, the high anionic character of polycondensates (e.g. BNS, MFS) favors an immediate and almost quantitative adsorption on cement. Consequently, the fluidity rapidly decreases within the first 30 min because no polymer remains in the pore solution to disperse newly formed hydration products. The adsorption properties of PCEs are influenced by the anionic charge amount and the side chain density. Principally, two generic types are differentiated (Fig. 2). PCE variants with a high side chain density and short side chains are favorable for ready mix concrete, whereas products with a high anionicity and a long side chain length are mainly used for precast concrete. The PCE with a low anionic charge amount initially adsorbs only in a small quantity (20%–30% of dosage). The reserve of polymer remaining in the pore solution can then gradually adsorb over time which leads to a long slump retention. Because of this mechanism, such PCEs require a relatively high dosage. Oppositely, PCEs for precast concrete adsorb in a high amount (70%–80%) which engenders a fast decrease of the initial fluidity due to a much smaller depot effect of the non-adsorbed polymers.

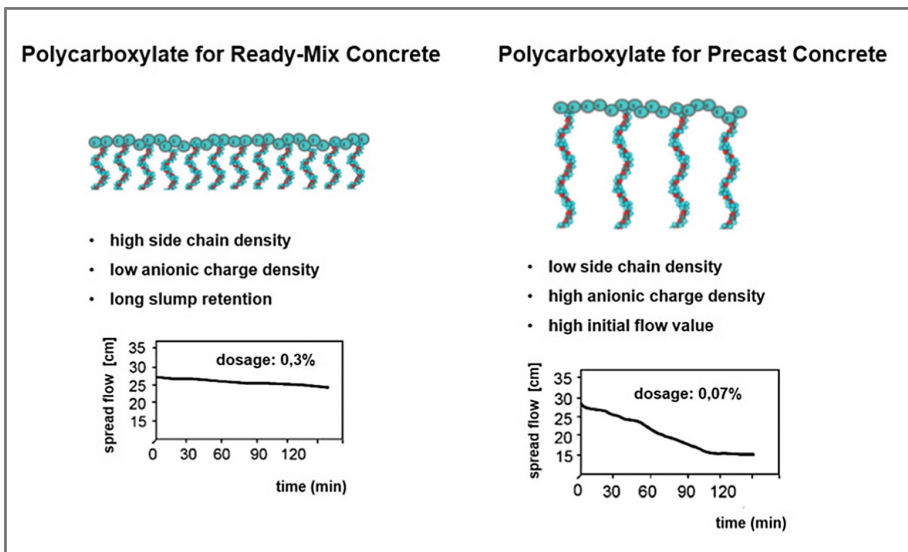


Fig. 2. Structural composition of PCEs applied in ready-mix and precast concrete.

3 Methods for Investigating Cement-Superplasticizer Interactions

Usually, the interaction of superplasticizers with cement is investigated by adsorption measurements using the depletion method. Here, the amount of polymer remaining in the pore solution after contact with cement at equilibrium condition is quantified by total organic carbon (TOC) analysis. Adsorbed amounts are determined for increasing polymer additions until a plateau value is reached (=saturated adsorption) signifying full surface coverage. Adsorption isotherms can be developed then by plotting the depleted amount of polymer as a function of the initial polymer concentration. The adsorption isotherms obtained for polycondensate and PCE based superplasticizers generally comply with the Langmuir adsorption model. However, it has to be noted that this analytical method is incapable of distinguishing the amount of polymer adsorbed via physical attraction from the portion which was consumed by absorption (=chemical intercalation) or precipitation. Therefore, data obtained from adsorption measurements should be interpreted in a prudent way since this method only gives an indication about the depleted amount of polymer.

Actual adsorption of superplasticizers can be corroborated by zeta potential measurements of cement slurries using the electroacoustic method. The zeta potential represents the electric potential at the shear plane between the Stern layer (stationary layer) and the diffuse ion layer of a colloidal particle. Though zeta potential does not correspond to the actual surface charge, it provides useful information about the colloidal stability and the working mechanism of superplasticizers. The typical zeta potential curves for a polycondensate and PCE based superplasticizer are illustrated in Fig. 3. As can be seen there, rising additions of the polycondensate gradually decreases the zeta potential to highly negative values (~ -55 mV) until to the saturated adsorption. At this point, the zeta potential remains constant because no polymer can adsorb on the surface anymore. The highly negative zeta potential induces an electrostatic repulsion of the cement particles.

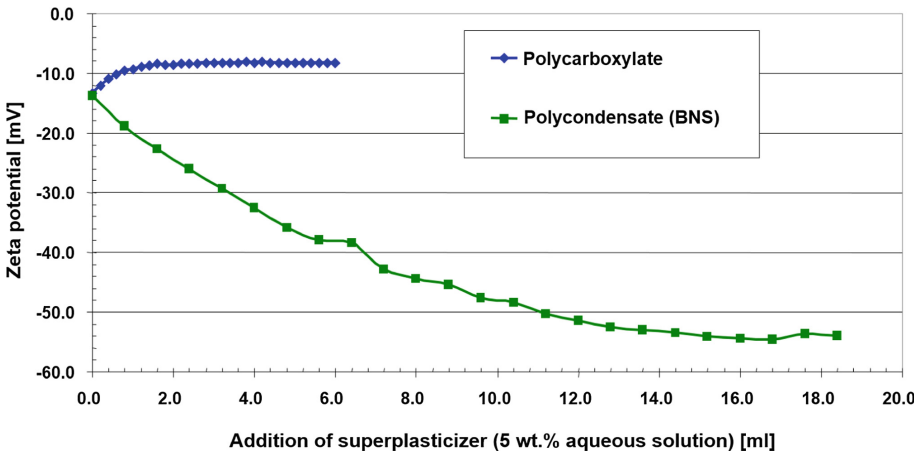


Fig. 3. Zeta potential of cement slurries admixed with different types of superplasticizers.

Adsorption of PCEs generally provokes an increase of the zeta potential. This can be attributed to a displacement of the shear plane by the polyethylene glycol side chains. PCEs with a long side chain length ($n_{EO} \geq 20$) move the shear plane to greater distances away from the cement surface thus causing a more positive value [9].

However, still the question remains on which surface areas superplasticizers adsorb. Yoshioka et al. found that a much higher quantity adsorbs on the aluminate phases (C_3A , C_4AF) than on the silicates (C_3S , C_2S) [2]. This was attributed to the different zeta potentials of the pure cement minerals. C_3A and C_4AF exhibit a positive zeta potential, whereas C_3S and C_2S develop a negative one. A further study revealed that also the adsorbed amount of superplasticizers on the surface of early hydration products is quite different [10]. High adsorbed amounts were especially found for those hydrate phases with a positive zeta potential (i.e. ettringite and mono sulfoaluminate). No adsorption occurred on syngenite, portlandite and gypsum because their zeta potential is zero or negative. This means that superplasticizers are mainly concentrated on surface areas where hydration products with a positive zeta potential crystallize. Thus, a mosaic structure results with an uneven distribution of the polymers on the surface area of the hydrating cement grain (Fig. 4) [10].

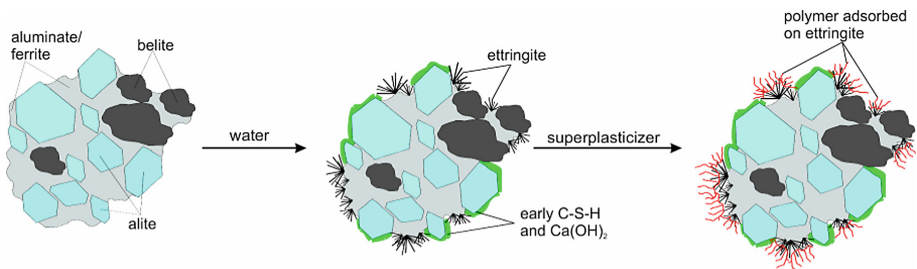


Fig. 4. Schematic presentation of the preferential adsorption sites of superplasticizers on a hydrating cement grain [10].

4 Chemisorption of Superplasticizers

Superplasticizers can interact with cement not only via surface adsorption, also intercalation (chemisorption) of a part of the polymer into the layered structure of calcium aluminate hydrates (C-A-H) may occur during cement hydration. This reaction is highly undesirable because after intercalation the polymer can no longer induce any fluidity. It was found that such intercalates (=organo-mineral phase) form instantaneously upon contact of cement with water when little or no sulfate is initially available for the hydration of C_3A [11]. For cements possessing a high content of alkali sulfates no intercalation was observed. The reaction patterns of C_3A are illustrated for different sulfate concentrations in Fig. 5. Generally, intercalation can be prevented by using alkali sulfates which immediately dissolve or by a delayed addition mode of the superplasticizer.

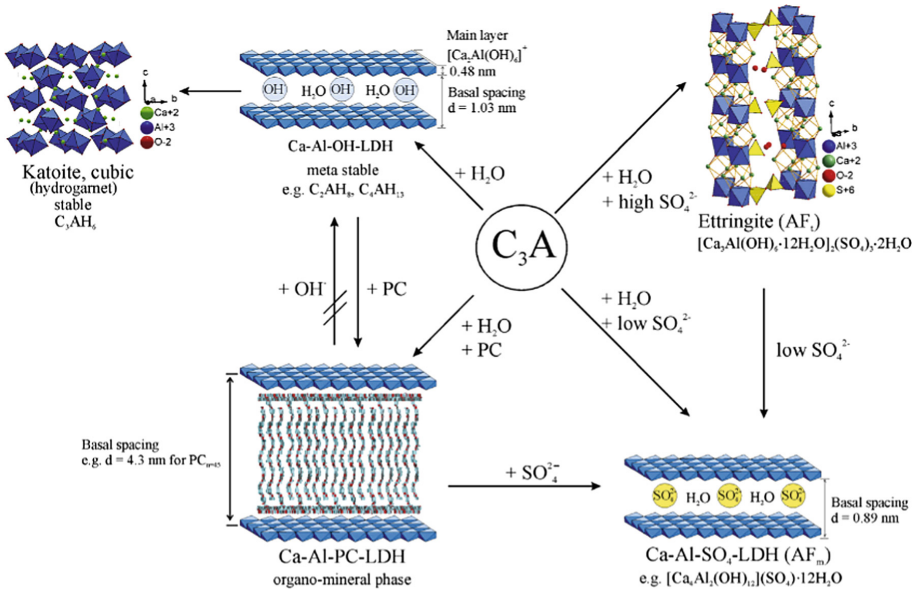


Fig. 5. Reaction patterns of C_3A hydrated at different sulfate concentrations in the absence and presence of a PCE superplasticizer [11].

5 Dispersion Forces at Low w/c-Ratios

Some studies suggest that at low w/c ratios the conventional models for dispersion like the DLVO theory and the Ottewill-Walker equation are no longer exclusively applicable. Instead, the portion of non-adsorbed polymers remaining in the pore solution seems to contribute to cement dispersion as well. This was first described by Sakai et al. who investigated the fluidity of low heat Portland cement – silica blends using different PCE superplasticizers at water-to-powder ratios from 0.16–0.32 [12]. According to their results, the paste fluidity at low w/p ratios (i.e. 0.16) cannot derive only from a steric effect of adsorbed PCE polymers, but is linked to non-adsorbed PCEs that remain in the pore solution. More recent studies showed that even specific non-ionic polymers and glycol compounds can augment the dispersing performance of PCEs at w/c ratios ≤ 0.30 [13]. It is assumed that such co-dispersants might induce repulsive depletion forces between the cement particles. However, more research is necessary to elucidate in more detail the role of non-adsorbed polymers to cement dispersion.

6 Summary

Superplasticizers can adsorb on cement, chemisorb into lamellar C-A-H phases or remain in the pore solution. The macroscopic properties of cement suspensions (e.g. rheology) are affected by those interactions. Adsorption of the superplasticizers on the

surface of the first hydration products is essential for cement dispersion. Depending on the chemical composition of the polymer dispersion is achieved by an electrostatic and/or steric effect. Chemisorption mainly occurs when cement is undersulfated. A low amount of highly soluble sulfates during the first seconds of the hydration of C_3A usually entails an intercalation of the superplasticizer into C-A-H phases. Thus, the polymer becomes ineffective and the fluidity decreases. However, non-adsorbed polymers that remain in the pore solution seem to contribute to cement dispersion especially at low w/c ratios.

References

1. Yoshioka K, Tazawa E, Kawai K, Enohata T (2002) Adsorption characteristics of superplasticizers on cement component minerals. *Cem Concr Res* 32:1507–1513
2. Yoshioka K, Sakai E, Daimon M, Kitahar A (1997) Role of steric hindrance in the performance of superplasticizers for concrete. *J Am Ceram Soc* 80:2667–2671
3. Flatt RJ (2004) Dispersion forces in cement suspensions. *Cem Concr Res* 34:399–408
4. Houst YF, Bowen P, Perche F, Kauppi A et al (2008) Design and function of novel superplasticizers for more durable high performance concrete (superplast project). *Cem Concr Res* 38:1197–1209
5. Flatt RJ, Schober I, Raphael E, Plassard C, Lesniewska E (2009) Conformation of adsorbed comb polymers dispersant. *Langmuir* 25(2):845–855
6. Hirata T, Ye J, Branicio P, Zheng J, Lange A, Plank J, Sullivan M (2017) Adsorbed conformations of PCE superplasticizers in cement pore solution unraveled by molecular dynamics simulations. *Sci Rep* 7:16599
7. Nylander T, Samoshina Y, Lindman B (2006) Formation of polyelectrolyte-surfactant complexes on surfaces. *Adv Colloid Interfac* 123–126:105–123
8. de Reese J, Plank J (2011) Adsorption of polyelectrolytes on calcium carbonate – Which thermodynamic parameters are driving this process? *J Am Ceram Soc* 94:3515–3522
9. Plank J, Vlad D, Brandl A, Chatziagorastou P (2005) Colloidal chemistry examination of the steric effect of polycarboxylate superplasticizers. *Cem Int* 2:100–110
10. Plank J, Hirsch C (2007) Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. *Cem Concr Res* 37:537–542
11. Plank J, Dai Z, Keller H, von Hoessle F, Seidl W (2010) Fundamental mechanisms for polycarboxylate intercalation into C_3A hydrate phases and the role of sulfate present in cement. *Cem Concr Res* 40:45–57
12. Ushiro M, Atarashi D, Kawakami H, Sakai E (2013) The effect of superplasticizer present in pore solution on flowability of low water-to-powder cement paste. *Cem Sci Concr Technol* 67:102–107
13. Lange A, Plank J (2016) Contribution of non-adsorbing polymers to cement dispersion. *Cem Concr Res* 79:131–136