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Contribution of non-adsorbing polymers to cement dispersion



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ABSTRACT

It has been noticed recently that at low w/c ratios (≤ 0.30), non-adsorbed polycarboxylate (PCE) polymers can contribute as well to cement dispersion. This study aimed at defining more specifically the structural requirement for such non-adsorbing polymers. For this purpose, a cement paste (w/c = 0.30) containing a conventional MPEG PCE superplasticizer was admixed with additional quantities of a polyester polymer prepared *via* homopolymerization of MPEG methacrylate ester macromonomer, the macromonomer used in the homopolymerization, and the polyethylene glycol contained in the macromonomer. It was found that when admixed individually, all three polymers do not adsorb on cement and cannot fluidize the paste but enhance dispersion and fluidity significantly when combined with the PCE superplasticizer. A potential explanation is that the non-adsorbing polymers act as lubricants between cement, which are particularly densely packed at low w/c ratios. The pore fluid loaded with non-adsorbed polymer exhibits superior lubrication compared to pristine cement pore solution.

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1. Introduction

Colloids represent a class of nano- and micrometer sized particles which exhibit some unique properties [1]. Among them is their ability to scatter light when dispersed in a medium, which is commonly referred to as the Tyndall effect [2]. Typical colloidal materials are the different kinds of clavs including bentonite, kaolinite, and attapulgite, as well as cement powder. When dispersed in water, colloids form suspensions exhibiting different viscosities depending on their particle size, density, pH-dependent surface charge, and the ionic strength of the aqueous phase. Cement dispersed in water produces an exceptionally high viscosity when compared with similar suspensions prepared from silica (SiO₂) or limestone (CaCO₃) powder of the same particle size. The reason behind is the heterogeneous surface charge of a cement particle stemming from the presence of different clinker phases (the aluminates C₃A and C₄AF exhibit a positive and the two silicate phases C_3S and C_2S a negative surface charge) [3]. Contrary to cement, SiO₂ or CaCO₃ possess homogeneous surface charges and thus do not much agglomerate in water via attraction of oppositely charged surface sites, as is the case for cement [4]. Therefore, to achieve a concrete or mortar of high fluidity and low viscosity, it is necessary to add a superplasticizing chemical admixture, which can disparage the large agglomerates into individual cement particles.

Generally, for the dispersion of particles in a medium, three principle mechanisms are being discussed in the literature: electrostatic, steric, and depletion stabilization [5,6].

(1) Electrostatic stabilization can be achieved when two particles exhibit the same electrical charge. This concept was introduced by *Derjaguin, Landau, Verwey*, and *Overbeek*, who independently worked on the stability of lyophobic colloids (oil/water emulsions) [7,8]. According to their model, which is now known as DLVO theory, the electrostatic repulsion potential is expressed by the equation as follows:

$$V_{\text{repulsive}}(d) = \frac{a \cdot 32 \cdot \varepsilon \cdot \varepsilon_0}{\sigma} \cdot \left(\frac{R \cdot T}{F}\right)^2 \cdot \gamma^2 \cdot e^{-\kappa d}$$
(1)

where *d* is the interparticle distance, *a* is the particle radius, ε is the permittivity, ε_0 is the permittivity of vacuum, σ is the charge of ions, *F* is *Faraday*'s constant, *R* is the universal gas constant, *T* is the temperature, and $\gamma = (e^{z/2} - 1) \times (e^{z/2} - 1)$.

The electrostatic repulsion between two particles strongly depends on the *Debye* length $1/\kappa$ and thus on the thickness of the diffuse ion cloud around a particle. Therefore, high ionic strength caused by high electrolyte concentrations as are present in cement pore solution reduce the repulsive force between particles [9].

It is commonly believed that polycondensate-based superplasticizers such as, e.g., β -naphthalensulfonate formaldehyde, melamine formaldehyde sulfite, or acetone formaldehyde sulfite predominantly achieve dispersion of cement *via* this mechanism,

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Table 1

Phase composition of the CEM I 52.5 N cement sample, as determined via quantitative XRD analysis including *Rietveld* refinement.

Phases	Content, wt.%
C ₃ S, m	53.95
C ₂ S, m	26.54
C ₃ A, c	3.26
C ₃ A, o	4.24
C ₄ AF, o	2.44
Free lime, Franke	0.10
Periclase	0.03
Anhydrite	2.63
Hemihydrate ^a	1.20
Dihydrate ^a	0.03
Calcite	3.59
Quartz	1.16
Arcanite	0.46
Sum	99.63

Determined *via* thermogravimetry.

although a partial steric effects is involved as well, as was evidenced from the thermodynamic parameters ΔG , ΔH , and ΔS for the adsorption of these polymers [10,11].

(2) Steric stabilization arises from polymers adsorbed on the surface of a colloidal particle and is considered to be more effective than electrostatic repulsion [12,13]. According to *Ottewill* and *Walker*, the steric repulsion potential between two particles is represented as follows [14,15]:

$$V_{\text{steric}}(d) = \frac{4 \cdot \pi \cdot k_b \cdot T \cdot C_V^2}{3 \cdot \vartheta^2 \cdot f_2^2} \cdot (\Psi_1 - \kappa) \cdot (\delta - d)^2 \cdot (3R + 2\delta + d/2)$$
(2)

where C_{ν} is the concentration of the adsorbed polymer, δ is the molecular volume of the solvent molecules, δ is the adsorbed layer thickness, f_2 is the density of the adsorbate (polymer), ψ_1 is the entropy, κ is the enthalpy, R is the radius of the adsorbate, and d is the distance between two adsorbate particles.

This model clearly suggests that the thickness of the adsorbed polymer layer, δ , plays a prominent role for stabilization as it impacts V_{steric} in the third power. The superior dispersing effect of polycarboxylate superplasticizers is commonly attributed to a strong steric effect arising from their extended side chains [16]. This is supported by the observation that PCEs exhibiting longer side chains represent more powerful dispersants than those with shorter side chains [17]. Unfortunately, at present, only data on the adsorbed layer thickness of PCE polymers obtained from atomic force microscopic (AFM) measurements are available, which are surprisingly low (1–4 nm) and might be specific for this test method [18]. More data from additional methods will be needed to gain a complete understanding of the dimensions of various adsorbed polymer layers.

Attempts have been made to quantify the total repulsive force resulting from the sum of electrostatic and steric (the "electrosteric") contributions by using AFM measurements [19–21]. It was found that PCEs can provide a much higher repulsive force than linear polycondensate-based superplasticizers, such as, e.g., naphthalene- or melamine-based ones. Furthermore, it was confirmed that the total repulsive force is dependent on the surface charge of the substrate and the ionic strength of the aqueous phase, as was predicted by theory.

(3) Depletion stabilization is assigned to non-adsorbing polymers when present in high concentrations in the dispersion phase. When particles approach each other at distances less than the radius of gyration, R_g of the polymers present, then the polymer molecules are depleted from the interparticle region. As a consequence, a concentration gradient develops which leads to an osmotic pressure and reduction in entropy. This way, depletion of the macromolecules is prevented [1]. This mechanism is considered for systems only which contain relatively high concentrations (2–3%) of water-soluble macromolecules [5,6]. Because of this condition, it does not seem to apply for cementitious systems admixed with superplasticizers because their dosages typically lie at 0.05–0.5% by weight of cement and thus are far below what the depletion mechanism requires to become effective.

To conclude, the current models on stabilization of colloidal systems suggest that for a concrete superplasticizer to be effective, it needs to include charged groups, which can facilitate its adsorption on cement and install an electrostatic repulsive force between particles, and possibly pendant groups, which can provide a steric dispersion effect.

The aim of the present research project was to investigate on earlier observations by the group of *Daimon* and *Sakai* [22,23] as well as our group [24] that non-adsorbed PCE polymers can also contribute to cement dispersion. This phenomenon cannot be explained by the existing theories as presented before. For this purpose, a cement paste fluidized with conventional MPEG PCE polymer was further admixed with three types of nonionic, non-adsorbing polymers: a polyester prepared by homopolymerization of the corresponding MPEG methacrylate ester macromonomer, the macromonomer as is, and a polyethylene glycol of a chain length as is present in the polyester and the macromonomer.



Fig. 1. Chemical structures of the PCE superplasticizers, of the macromonomer and of methoxy poly(ethylene glycol) used in the tests.

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