



Dispersing performance of superplasticizers admixed to aged cement



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HIGHLIGHTS

- Ageing of cement and binary mixtures of C_3A and gypsum was studied.
- Effect of aged cement on dispersing performance of different PCEs was investigated.
- Dispersing effectiveness of PCEs can decrease or improve in aged cement.
- Effect is controlled by agglomeration and progressing ettringite formation.
- Concentration and kind of polymorph of C_3A determines the effect of ageing on PCE.

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ABSTRACT

A mechanistic study using fresh and aged binary mixtures of C_3A (cubic and orthorhombic) and gypsum revealed that the interaction and hence dispersing performance of superplasticizers in aged cement is controlled by two competing processes, one being agglomeration and caking of the binder particles resulting in a decreased specific surface area, and the other process being continuous formation of hydration products, especially of ettringite, which leads to an increase of surface area. The results suggest that the interaction of superplasticizers with aged cement can be positive or negative, depending on the composition of the cement relative to C_3A , with negative effects being most prevalent.

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1. Introduction

Ageing of cement is a consequence of its reaction with water vapor and potentially atmospheric CO_2 . It can start already during cement production, where sometimes water is sprayed into the clinker mill for cooling purposes, or in the silo where gypsum can dehydrate as a result of high clinker temperature [1]. As a result of such exposure to humidity, changes in the setting and hydration behavior, strength development, rheological properties and, consequently, a rapid loss of workability of cement and dry-mix mortars were observed [1–4].

The physicochemical effects of water sorption on individual clinker phases as well as different sulphates (gypsum, hemihydrate and anhydrite) and free lime have been thoroughly investigated and are described in a series of articles [5,6]. There it was observed that at very different levels of relative humidity (so-called “threshold values”), the individual clinker phases start to sorb water. The most hygroscopic phase was found to be free lime whose sorption already begins at 14% relative humidity (RH). This phase is fol-

lowed by hemihydrate (sorption beginning at 34% RH) and orthorhombic C_3A (55% RH). Surprisingly, cubic C_3A starts to sorb water only at 80% RH, suggesting that orthorhombic C_3A is significantly more reactive than the cubic polymorph [7]. In comparison, the silicate phases C_3S and C_2S sorb water above 63% (C_3S) and 64% (C_2S) RH, respectively. This study also revealed that the sorbed water can be bound to the cement/clinker surfaces physically (which is reversible), chemically (irreversible) or in both ways. Chemical sorption leads to the formation of nano-scale hydration products on the surface of cement and alters its surface charge and specific surface area. These changes can have a significant impact on the effectiveness of chemical admixtures [8].

In another article Winnefeld [9] has presented that cement ageing can negatively impact on the setting behavior and the early strength of cements, whereas regarding the flow behavior of pastes prepared from such aged cement a slight improvement was observed. The same study also revealed that polycondensate and polycarboxylate superplasticizers performed even better with such aged cement, surprisingly in spite of a decrease of their adsorbed amounts. These results appear to be in contradiction to those from [8] which report that the effectiveness of a polycondensate (BNS) and a PCE-based superplasticizer decreases in aged cement.

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This study was performed to investigate the mechanism behind the impact of cement ageing on superplasticizer performance. For this purpose, a CEM I 52.5 N was aged at 35 °C/90% relative humidity for 1 and 3 days. Thereafter, the dispersing performance of three different types of powdery superplasticizers (BNS, PCE and casein) was tested with aged cement. In a mechanistic study, the fresh and aged CEM I 52.5 N as well as binary mixtures of C₃A (cubic and orthorhombic) and gypsum were looked at. Their particle size, zeta potential and powder X-ray diffraction diagrams were analyzed and their surface properties determined. As superplasticizers, two methacrylate ester and two allylether-type PCEs were used. Their dispersing effectiveness was assessed via mini slump tests on cement paste, and their interaction with cement and the binary mixtures was quantified via adsorption tests. From the results it was hoped to develop a model explaining the sometimes negative or positive impact of cement ageing on the dispersing performance of superplasticizers which also has been observed and reported by applicators.

2. Experimental

2.1. Raw materials

The experiments were performed with a CEM I 52.5 N (Milke® “classic”, Geseke plant, HeidelbergCement AG, Germany). The phase composition of this cement as presented in Table 1 was obtained by quantitative X-ray diffraction (Rietveld method). Its specific density was 3.15 g/cm³ (He pycnometry) and its specific surface area (Blaine method) was found at 3560 cm²/g.

For the mechanistic study, C₃A clinker phases (cubic and orthorhombic) were synthesized from CaCO₃ (Merck KGaA, Darmstadt/Germany) and Al₂O₃ (Nabalox 325, Nabaltec, Schwandorf/Germany) following a description by Wesselsky and Jensen [10]. In the preparation of cubic, non-doped C₃A, CaCO₃ and Al₂O₃ at a molar ratio of 3:1 were finely powdered and homogenized using a ball mill (Pulverisette, Fritsch, Idar-Oberstein/Germany). The homogenized mixture was transferred to a platinum crucible and placed in an oven which was heated within 12 h to 1300 °C. This temperature was held for 12 h until the platinum crucible was allowed to cool in the oven before removal. The cooled sample was then finely ground using the ball mill from above.

To obtain orthorhombic C₃A, doping with sodium carbonate was performed (5 wt.-% Na₂O). After homogenization in the ball mill, the mixture was heated in the platinum crucible for 5 h at 1300 °C. The platinum crucible was then removed from the oven and rapidly cooled using an air flow. Calcination was repeated three to four times until XRD confirmed formation of C₃A_o to be complete.

Table 1
Phase composition of the CEM I 52.5 N sample.

Phase	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, Rietveld	0.36
Free lime, Franke	0.14
Periclase	0.03
Anhydrite	2.63
Hemihydrate (TGA)	1.20
Dihydrate (TGA)	0.03
Calcite	3.59
Quartz	1.16
Arcanite	0.46
Sum	100.04

To study ettringite formation, the cubic and orthorhombic C₃A samples, respectively, were mixed with gypsum (Merck KGaA, Darmstadt/Germany) at a weight ratio of 1: 1.

Deionized water used for the cement/clinker hydration experiments was obtained from a Barnstead Nanopure™ Diamond device (Werner Reinstwassersysteme, Leverkusen, Germany).

2.2. Superplasticizer samples

The mechanistic study with fresh and aged CEM I 52.5 N and with binary mixtures of C₃A/gypsum, two methacrylate ester- and two allylether-type PCEs were used. Their chemical structures are displayed in Fig. 1. The MPEG-PCEs denoted as 45PC2 and 45PC6 were synthesized by copolymerizing methacrylic acid with methoxy polyethylene glycol methacrylate macromonomer [11]. Molar ratios of methacrylic acid: methacrylate ester of 2:1 and 6:1 were used and the side chain of the comb polymers consisted of 45 ethylene oxide (EO) units. The APEG-PCEs denoted as 23P1.5 and 70P1.5 were copolymerized in bulk using benzoyl peroxide as initiator [12]. They exhibited side chains made of 23 and 70 EO, units respectively. The characteristic molecular properties of the PCE polymers as evidenced by gel permeation chromatography (GPC) and their specific anionic charge densities are displayed in Table 2. Note that in all tests performed in this study, the superplasticizer samples were generally dissolved in the mixing water used to prepare the cement or C₃A/gypsum pastes.

2.3. Ageing of the samples

Ageing in this study was performed at 35 ± 2 °C and 90 ± 5% relative humidity in a climate chamber (Fig. 2, left). These conditions were chosen because most problems with shelf-life stability occur in hot and humid climates and they present an accelerated ageing scenario for less severe climate conditions. The fresh samples (CEM I 52.5 N, C₃A_{c/o}/gypsum with and without superplasticizer powder) were spread out in a thin layer of about 1 mm thickness on a 60 × 135 cm Plexiglas® plate (~220 g per plate) (Fig. 2, right). Depending on the sample, storage periods were 1, 3, 7 or 14 days. During ageing the cement powders solidified into sheets which were easily broken by shaking in a PE bottle.

2.4. Analytical methods

The fresh and aged samples were analyzed via powder X-ray diffraction by using a D8 Advance X-ray instrument (Bruker AXS, Karlsruhe/Germany) equipped with a CuK_α X-ray source. The samples were scanned in a range from 5 to 70° 2θ. Scanning electron microscopy (SEM) imaging was performed using a XL30 ESEM FEG microscope (FEI, Eindhoven/Netherlands).

Particle sizes (d₅₀ values) were measured in isopropanol as solvent using a laser granulometer (Cilas 1064, Quantachrome, Odelzhausen/Germany). Ultrasonication was applied to avoid reversible particle agglomeration.

Zeta potential measurements of the C₃A/gypsum blends were performed on a Model DT-1200 electroacoustic spectrometer (Dispersion Technology Inc., Bedford Hills, NY/USA). Due to the high water demand of the aged C₃A samples, a water-to-solid ratio of 40 was applied.

Dispersing performance of the superplasticizers was assessed using a modified “mini slump” test based on DIN EN 12706 [13]. There, a small brass cylinder (diameter 14 mm/height 25 mm) was used. The pastes (5 g solid, w/s = 1, mixing for 2 min) were filled to the brim of the cylinder. Afterwards, the cylinder was lifted vertically from the glass plate. The resulting spread of the paste was measured twice, the second measurement being perpendicular to

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