



Formation of organo-mineral phases at early addition of superplasticizers: The role of alkali sulfates and C₃A content

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ABSTRACT

Most superplasticizers (SPs) exhibit significantly higher dispersing performance when added to an already mixed concrete (delayed mode) instead of addition with mixing water (early addition). Here, the specific parameters which determine this effect were investigated. At first, the tendency of four polycarboxylates and a naphthalene-polycondensate to intercalate into C₃A hydrates was correlated with the flow values of pastes prepared from six different commercial cements at early and delayed addition. It was found that the contents of alkalisulfates and C₃A present in the cement samples play the key role. For cements exhibiting a low alkalisulfate/C₃A molar ratio (0.04–1.29), huge differences in paste flow at early and delayed addition were observed, presumably because of chemisorption (intercalation) of SP into C₃A hydrates. While at high alkalisulfate/C₃A molar ratios (~2), AF_i (ettringite) is formed predominantly, and SP intercalation is impossible. Consequently, similar flow values are attained at early and delayed addition.

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1. Introduction

Modern concrete technology requires high performance admixtures in order to fulfill the demands of excellent workability and high compressive strength after hardening [1]. Superplasticizers (SPs), either based on polycondensate or polycarboxylate ether (PCE) chemistry, allow to produce a highly flowable concrete and/or to reduce the water/cement ratio of concrete, resulting in higher compressive strength and improved durability. For those applications, it is essential to profoundly understand the interactions occurring between the SPs and the mineral components formed during cement hydration. It is generally accepted that high water reduction and high fluidity of concrete containing SP are attributed to the polymer molecules adsorbing onto the surface of cement particles [2,3]. In this way, a polymer layer exercising an electrostatic and/or steric effect between the cement particles is formed [4,5]. As a result, interparticle attraction is reduced and flowability of the dispersion is achieved.

Numerous studies conclude that Portland cement possessing high C₃A content interacts particularly strong with SPs [2–4,6–8]. Especially for high performance concrete where the effectiveness of the SP plays a most critical role, this interaction with C₃A has led to the recommendation to only use Portland cement with low content of C₃A (<3 wt.%). Furthermore, Aitcin et al. report that the compatibility between cement and SP strongly depends on the amount of soluble alkali present in

cement. They found that in low-alkali cements, the amount of C₃A significantly influenced the adsorption of a naphthalene sulfonate (BNS) dispersant, while in high-alkali cements, the C₃A content had essentially no effect on the dispersing performance of BNS. They concluded that the content of soluble alkali presents a key parameter for compatibility between cement and SP [9,10].

The hydration of C₃A and tetracalcium alumoferrite (C₄AF) present in cement produces hydrocalumite-type layered double hydroxides (LDHs) which can intercalate various anions in between their cationic main layers. For example, the layered phases C₂AH₈ and C₄AH₁₃ are formed by intercalation of OH⁻ anions [11]. They are metastable compounds which within minutes or hours convert to the cubic phase katoite, C₃AH₆, the thermodynamically most stable modification of the calcium aluminate hydrates at room temperature. Sulfate which is commonly present in any ordinary Portland cement (OPC), e.g. in the form of gypsum, to control its setting behavior, may intercalate into the layered calcium aluminate hydrates as well, resulting in [Ca₄Al₂(OH)₁₂](SO₄)·6H₂O (AF_m or monosulfoaluminate) [12]. Some years ago it has been found that also anionic polymers which are applied as concrete admixtures can intercalate into the lamellar calcium aluminate hydrates. From the group of SPs, β-naphthalene sulfonate formaldehyde condensate (BNS) was the first for which intercalation was reported [13]. Recently, we could demonstrate the formation of calcium aluminum layered double hydroxides incorporating PCE superplasticizers (Ca-Al-PCE-LDHs). They were obtained by rehydration of C₃A in aqueous PCE solution [14,15]. According to this study, the ability of PCEs to intercalate increases with higher anionic charge density and shorter side chain. PCEs possessing side chains containing up to 45 ethylene oxide units (EOUs) were found to intercalate easily whereas a PCE with 111 EOUs hardly

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intercalates. Besides the steric size of PCE, sulfate is another factor determining the extent of PCE intercalation. At high $\text{SO}_3/\text{C}_3\text{A}$ ratios in cement (e.g. >2), sulfate, because of its higher specific anionic charge density in comparison to PCE, will occupy the interlamellar space and thus prevent intercalation of the polymer. Thus, in this study PCE intercalation was found to occur only at $\text{SO}_3/\text{C}_3\text{A}$ ratios at or below 1 [16]. Note that here SO_3 stands for the total amount of SO_3 contained in a cement sample (the sum of SO_3 from calcium and alkali sulfates). The conformation of intercalated PCE molecules was investigated by another group [17]. They found that the side chains of PCE comb polymers form blobs (half-spheres) which are filling the interlayer space.

Another well known effect in concrete technology is that some SPs show great differences in their performance, depending on the time of addition to concrete. Typically, delayed addition (*i.e.* SP addition to an already mixed concrete) produces higher concrete flowability than early addition (*i.e.* SP addition in the mixing water). It has been observed that this effect occurs only for combinations of certain SPs and cements, that it can be more or less pronounced, and it may not show at all. No conclusive experimental data has been presented so far to explain this phenomenon. In a brilliant article published in 2001, Flatt and Houst presented numerous data from concrete testing which suggest that interaction of SPs with hydrating cement not only involves surface adsorption, but may include as well the formation of organo-mineral phases resulting from SP intercalation into lamellar calcium aluminate hydrates [18]. According to them, chemical absorption of SPs occurring during the very first seconds of cement hydration could explain the difference in SP performance at early and delayed addition. The authors also point out that sulfate may play a key role in this process.

Obviously, if SPs are intercalated, then they are no longer available for the superplasticizing effect which requires surface adsorption on the cement grains. In such case, a higher dosage of SP will be required to compensate the polymer lost by chemical absorption.

The aim of our study was to correlate experimental data on the intercalation ability of SPs with their fluidizing effect upon early and delayed addition to cement paste. For this purpose, we selected six commercial cements possessing different contents of C_3A , total SO_3 and alkali SO_3 . We then tested the spread flow values of those cement pastes after immediate and delayed addition of four PCE samples possessing various side chain lengths. A BNS polycondensate was chosen for comparison. It was hoped that the different intercalation tendency of these SPs as determined in a previous study could provide a mechanistic explanation for the differences in their dispersing performance observed at different times of addition. Furthermore, the chemical composition of the cement samples was correlated with the flow behaviors.

2. Materials and methods

2.1. Cement samples

Six commercial cement samples obtained from different sources in Germany (Table 1) were used. Their phase composition is shown in Table 2. The phase contents were determined by X-ray diffraction (XRD) using Rietveld refinement (Bruker D8 advance instrument, Bruker-AXS, Karlsruhe, Germany). Only the contents of gypsum and hemihydrate were determined by differential scanning calorimetry

Table 1

Type and source of the commercial cement samples used in the study.

Cement sample	Type	Producer
#1	CEM I 52.5 R	Schwenk Cement KG, Heidenheim plant
#2	CEM I 32.5 R	HeidelbergCement, Rohrdorf plant
#3	CEM I 52.5 N	HeidelbergCement, Geseke plant
#4	CEM I 32.5 N-LH/HS	Schwenk Cement KG, Allmendingen plant
#5	CEM I 52.5 R HS/LA	Holcim, Lägerdorf plant
#6	CEM I 52.5 N-HS-LA	HeidelbergCement, Paderborn plant

Table 2

Phase compositions of the six commercial cement samples studied.

Phase (M-%)	Cement sample					
	#1	#2	#3	#4	#5	#6
Alite	68.1	60.4	67.2	45.1	70.3	58.0
Belite	14.6	11.1	14.0	26.2	12.0	16.4
C_3A cubic	7.3	3.4	8.4	1.9	0.6	1.4
C_3A orthorhombic	1.2	5.9	0.0	0.0	0.5	0.0
C_4AF	3.9	7.3	2.7	17.1	12.5	15.3
Calcite	0.0	2.6	3.8	1.6	0.6	0.0
Periklase	0.0	2.0	0.0	0.0	0.0	0.0
Gypsum	0.0	0.0	0.0	0.3	0.2	0.9
Hemihydrate	3.1	1.3	0.0	1.5	1.8	0.4
Anhydrite	1.8	3.1	2.4	3.6	0.3	3.1
Dolomite	0.0	0.6	0.0	0.0	0.0	0.0
Lime	0.0	1.2	0.1	0.0	0.0	0.4
Quartz	0.0	0.3	0.8	0.1	0.0	0.0
Total SO_3	2.60	2.90	2.35	3.40	1.93	3.00
Alkali SO_3	0.10	0.70	1.23	0.72	0.68	0.85
Total $\text{SO}_3/\text{C}_3\text{A}$ [m. r.] ^a	1.05	1.04	0.94	6.04	5.90	7.23
Alkali $\text{SO}_3/\text{C}_3\text{A}$ [m. r.] ^a	0.04	0.25	0.50	1.29	2.09	2.05
w/c ratio ^b	0.57	0.56	0.55	0.44	0.47	0.53

^a m. r. = molar ratio.

^b Required to obtain a paste spread of 18 ± 0.5 cm in 'mini slump' test.

(DSC 200 F3, Netzsch, Selb, Germany) using the pure phases for calibration. The content of alkali sulfates was calculated as difference between the total SO_3 content contained in the cement sample as obtained from X-ray fluorescence (XRF instrument Axios from PANalytical, Philips, Eindhoven, the Netherlands) and the cumulated SO_3 content present in gypsum, hemihydrate and anhydrite as obtained by TG/XRD analysis. The molar ratios of $\text{SO}_3/\text{C}_3\text{A}$ were established from the total SO_3 content of the cement samples and the C_3A content determined by Rietveld analysis.

The selected cements represent differences in the C_3A contents varying from as low as 1.1 M-% up to 9.3 M-%, as well as in the alkali sulfate contents (expressed as SO_3) ranging from 0.1 M-% to 1.23 M-%. The total $\text{SO}_3/\text{C}_3\text{A}$ molar ratios vary between 0.94 (sample #3) and 7.23 (sample #6).

2.2. Superplasticizer samples

The superplasticizers used were different methacrylic acid – ω -methoxy poly(ethylene glycol) methacrylate ester copolymers with side chain lengths of 8.5; 17; 45 and 111 ethylene oxide units (EOUs), respectively, and a molar ratio of methacrylic acid:methacrylate ester of 6:1. Synthesis and characteristic properties (molar masses, polydispersity index, etc.) of these polymers were described in a previous work [14]. Moreover, a BNS polycondensate (Melcret[®] 500 F, a commercial product from BASF Construction Polymers GmbH, Trostberg/Germany) was tested as well. The chemical structures of the SPs are presented in Fig. 1.

2.3. Paste flow tests

For all cements, pastes were prepared at the specific w/c ratios producing a flow value (spread) of 18 ± 0.5 cm (*mini slump test*). As early addition, SP was added to the mixing water. The SP dosage was chosen to produce a flow value of 26 ± 0.5 cm. In a typical experiment, cement powder was poured into the mixing water and let to soak for 2 min without agitation. Then the blend was mixed manually for 2 min to obtain a well-dispersed paste. Thereafter, the paste was poured into a Vicat cone (top diameter 6 cm, bottom diameter 7 cm, height 4 cm). The cone then was removed and the diameter of the spread cement paste was measured. Testing was carried out at a temperature of 23 ± 1 °C. Generally, the amount of water introduced from addition of the SP solution was subtracted from the amount of mixing water to maintain a constant w/c ratio for each cement sample. The SP dosage in the mix is

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