Impact of zeta potential of early cement hydration phases on superplasticizer adsorption

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Abstract

The zeta potential of early hydration products of cement was found to be a key factor for superplasticizer adsorption. A highly positive zeta potential results in a strong superplasticizer adsorption whereas a negative zeta potential does not allow adsorption. Synthetic ettringite precipitated from solution shows a highly positive zeta potential, hence it adsorbs great amounts of negatively charged superplasticizer. Monosulfate (AF_m) has a less positive zeta potential. Therefore, it adsorbs smaller amounts of superplasticizers. For syngenite, portlandite and gypsum, the zeta potential is around zero or negative. These phases do not adsorb superplasticizers. Consequently, a hydrating cement grain is best represented by a mosaic structure, with superplasticizer molecules mainly adsorbed on ettringite and some on monosulfate and C–S–H nucleated at surface.

1. Introduction

The interaction between superplasticizers and cement is still under investigation. Major aspects are whether superplasticizers adsorb evenly on the surface of a hydrating cement grain, and whether superplasticizers are not only adsorbed, but also absorbed. Cement grains show a mosaic surface resulting from the different clinker phases. Previous studies of superplasticizer adsorption on the pure cement clinker phases C_3S, C_2S, C_3A and $C_2(A,F)$ revealed that much higher adsorption occurs on the aluminate and ferrite than on the silicate phases [1]. Earlier studies on C–S–H phases conclude that their initial zeta potential is negative, but may become positive as the Ca^{2+} concentration in the cement pore solution increases and adsorption of Ca^{2+} on the C–S–H phases occurs [2–4]. Hence, superplasticizers may also adsorb onto C–S–H phases. Due to the high specific surface area of C–S–H (approx. 300 m^2/g), however, the amount of polymer adsorbed per unit area is relatively small (approx. 0.2 mg/m^2). Several authors

have shown that superplasticizers may adsorb also on inert powders which are added to concrete or dry-mix mortars as fillers or aggregates. Examples of such powders are fly ash, limestone [5], silica fume [6] and clays [7]. The reason for adsorption being electrostatic interaction between the admixtures and the charged surfaces of these powders.

For superplasticizer effectiveness, adsorption on early cement hydration products such as ettringite ($[Ca_6Al_2(OH)_{12}](SO_4)_3 \cdot 26H_2O) = AF_t$), monosulfate ($[Ca_4Al_2(OH)_{12}](SO_4) \cdot 6H_2O = AF_m$), syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$), portlandite ($Ca(OH)_2$) and gypsum ($CaSO_4 \cdot 2H_2O$) appears to be particularly significant. Several authors have described single aspects of superplasticizer interaction with ettringite. Among them are studies on the amount of ettringite produced in the presence of superplasticizer [8], on the influence of β-naphthalene sulfonate formaldehyde (BNS) and lignosulphonate on ettringite formation [9,10], and on BNS adsorption on initial ettringite crystallites [11]. Intercalation of BNS into a layered calcium aluminate phase has been shown as the first example of superplasticizer absorption by a cement phase [12]. Most recently, intercalation of polycarboxylate superplasticizers into a C_3A hydration product also has been described [13–15]. It was found that C_3A hydrating in aqueous

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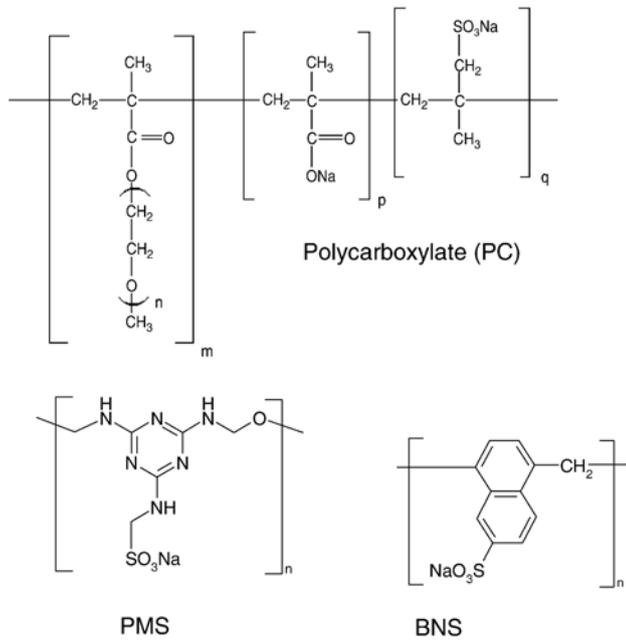 *E-mail address:* sekretariat@bauchemie-tum.de (J. Plank).

Fig. 1. Molecular structure of superplasticizers.

polycarboxylate solution may partially incorporate the anionic superplasticizer in between its $[Ca_2Al(OH)_6]^+$ main layers. The result is an organo-mineral phase with layered structure similar to those of C_2AH_8 and C_4AH_{13}, resp., but with a much wider interlayer distance because of the comb polymer. Thus, surface adsorption and incorporation into the crystal structure (chemisorption) are two principal ways of interaction between an admixture and cement.

Upon contact with water, an electrochemical double layer is formed on the surface of cement particles [16]. The electric charge on the surface of the hydrate phase depends on the chemical nature of the phase and the ions in the cement pore water. Major differences with respect to the sign and absolute value of hydrate phases can be expected. Superplasticizer adsorption is possible only when the particle charge is positive, or when the superplasticizer molecule desorbs an already adsorbed anion (e.g. OH^- or SO_4^{2-}).

The main purpose of this study was to investigate the influence of the zeta potential of early cement hydration products,

particularly ettringite, monosulfate, syngenite, portlandite, and gypsum, on superplasticizer adsorption. For this purpose, these hydrate phases were synthesized and their zeta potential was measured by using an instrument based on the electroacoustic method. It is capable of measuring at water/solids concentrations of approx. 0.5, thus simulating realistic conditions in a cement paste. To study the impact of chemical structure of superplasticizer molecules on adsorption, polycondensates based on melamine and naphthalene chemistry and polycarboxylates based on methacrylic acid/ω-methoxy poly(ethyleneglycol)methacrylate ester copolymer were synthesized.

2. Experimental

Ettringite was synthesized under N_2 atmosphere from solution according to Struble [17] by combining aqueous solutions of aluminium sulphate and lime in stoichiometric quantities. Syngenite was precipitated by combining solutions of $CaCl_2$ and K_2SO_4 (3 h, 40 °C), whereas monosulfate was formed in a suspension of monocalcium aluminate ($CaO \cdot Al_2O_3$), calcium oxide and anhydrite ($CaSO_4$) at 0 °C for two days and additional 3 month storage at room temperature. To obtain portlandite, freshly calcined calcium oxide was dispersed in water, yielding an active suspension of 0.6 wt.% $Ca(OH)_2$. For adsorption on gypsum, 99.7% pure grade $CaSO_4 \cdot 2H_2O$ was suspended in water to obtain a 1 wt.% active slurry. BET (N_2) specific surface areas were measured by continuously drying the crystalline material for 12 h in a desiccator (silica pearls) under constant N_2 stream at room temperature. Heating was avoided because of potential decomposition of the phases.

The zeta potential of the hydration phases was measured from the suspensions as obtained in the synthesis process (ettringite, monosulfate), or from the aqueous suspensions as above ($Ca(OH)_2$, gypsum). The value of the zeta potential was calculated from the colloidal vibration current (CVI) which was determined by electroacoustic measurement, performed by using a DT 1200 instrument from Dispersion Technology [18,19].

Chemical composition, molecular structure, molar masses (M_w, M_n) and anionic charge densities of the self-prepared superplasticizers are given in Fig. 1 and Table 1, respectively. Molar masses were obtained by gel permeation chromatography (GPC) using Waters Alliance 2695, pre column Ultrahydrogel, main columns OH Aquagel 120, 150 and 500; eluent 0.1 m

Table 1
Chemical composition, analytical data and dosage of superplasticizers

SP	Melamine:CH$_2$O:sulfite resp. β-naphthalene-sulfonic acid: CH$_2$O			M_w [Da]	M_n [Da]	Polydispersity index M_w/M_n	Anionic charge density 10^{-6} Eq/g	Dosage [wt.%]
PMS	1:3:1			102,920	20,390	5.05	4110	0.25
BNS	1:1.2			118,800	–	–	3780	0.25
	Methacrylic acid (p)	MPEG Methacrylate ester (m)	Methallyl sulfonic acid (q)	M_w [Da]	M_n [Da]	M_w/M_n	Anionic charge density 10^{-6} Eq/g	Dosage [wt.%]
PC-a	3	0.5	0.2	74,400	39,100	1.90	1340	0.04
PC-b	3	1	0.2	81,500	42,800	1.90	980	0.10
PC-c	3	2	0.4	74,500	47,300	1.58	430	0.19

Table 2
Zeta potential, BET surface and adsorbed amount of superplasticizer on early cement hydration phases

Hydration phase	Zeta potential [mV]	BET [m²/g]	Adsorption of superplasticizer															
			PMS			BNS			PC-a			PC-b			PC-c		
			Adsorbed amount			Adsorbed amount			Adsorbed amount			Adsorbed amount			Adsorbed amount		
			mg/g	mg/m²	%	mg/g	mg/m²	%	mg/g	mg/m²	%	mg/g	mg/m²	%	mg/g	mg/m²	%
Ettringite	+4.15	5.4	111	20.56	43	113	20.93	44	28	5.19	45	27	5.00	26	17	3.15	15
Monosulfate	+2.84	5.3	29	5.47	12	27	5.09	11	11	2.08	29	14	2.64	13	12	2.26	6
Syngenite	+0.49	4.7	0.37	0.08	15	0.20	0.04	8	0.05	0.01	14	0.12	0.03	12	0.13	0.03	7
Portlandite	−4.40	n.d.	–	–	0	–	–	0	–	–	0	–	–	0	–	–	0
Gypsum	−0.06	n.d.	–	–	0	–	–	0	–	–	0	–	–	0	–	–	0

NaNO$_3$, pH 12 (NaOH). The side chain length (number of ethylenoxide units, n_{EO}) of all polycarboxylates was 45. M_w for BNS was obtained by batch measurement because it cannot be chromatographed. In aqueous systems, it is retained in the column. Anionic charge density of all superplasticizers was determined in cement pore solution by polyelectrolyte titration using cationic poly(DADMAC) as titrator.

Superplasticizer adsorption on ettringite was determined under two different conditions: (a) addition of superplasticizer at the beginning of the crystallization process. This experiment simulates ettringite crystallization in a superplasticizer treated cement slurry; or (b) after completion of the hydration phase synthesis (2 h). This experiment simulates delayed superplasticizer addition. The dosage of the superplasticizers varied depending on its effectiveness in plasticizing cement paste (see Table 1). The unbound water was recovered by centrifugation of the slurry. Superplasticizer content in the filtrate was measured by TOC analysis using a High TOC II from Elementar (Hanau, Germany). Adsorption was calculated by subtracting superplasticizer concentration in the filtrate from initial superplasticizer concentration.

3. Results and discussion

Table 2 presents the zeta potentials and BET surface areas of the pure early hydration phases. With a zeta potential of + 4.15 mV, ettringite has by far the highest positive value for all phases. Its BET surface area was found to be 5.4 m²/g. Because of this positive zeta potential, ettringite should have the highest potential to adsorb negatively charged superplasticizers. A positive zeta potential of +2.84 mV, though not as high as for ettringite, was measured for monosulfate. Its surface area (5.3 m²/g) is comparable with ettringite. The zeta potentials for all other hydration products are either almost zero or negative, giving no favourable combination for the adsorption of negatively charged superplasticizers via electrostatic attraction. It should be noted that the absolute zeta potential values of the phases may vary during the precipitation process and also when formed from different cements. The reason being that it depends on the concentration of potential determining ions which will vary with cement composition and during the hydration process.

The adsorption data of different superplasticizers on ettringite, monosulfate and syngenite is presented in Table 2.

The adsorption of superplasticizers on portlandite and gypsum was negligible (<5%). The data allows the conclusions as follows:

1. The adsorbed amount of superplasticizer strongly depends on the existence of a positive zeta potential of the hydration phase. Therefore, ettringite is able to adsorb high quantities of negatively charged superplasticizers. Mineral phases with a zeta potential around zero or even a negative zeta potential do not adsorb significant amounts of superplasticizers.
2. High surface area by itself does not lead to adsorption if the zeta potential is negative or only slightly positive. Thus, a positive zeta potential is a key factor for adsorption.
3. At comparable specific surface area, ettringite shows 2–4 times more polymer adsorbed per surface area than monosulfate.
4. Generally, the adsorbed amount of polycondensates (in mg/g or mg/m²) is much higher than for polycarboxylates (approx. 20 vs. 3–5 mg/m² on ettringite). This is in line with the experimentally determined anionic charge densities of the superplasticizers. It confirms that polycondensates achieve its dispersion capability mainly through electrostatic repulsion mechanism.
5. The adsorption ratio of polycarboxylates also depends on their anionic charge density: the higher this charge density,
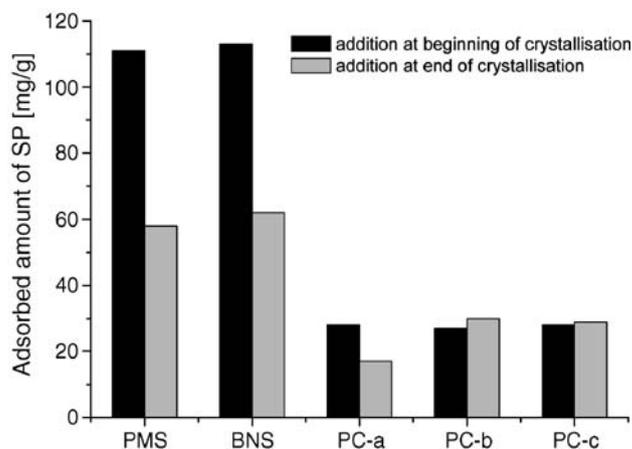

Fig. 2. Adsorbed amounts of superplasticizers on ettringite in case of early and delayed addition.
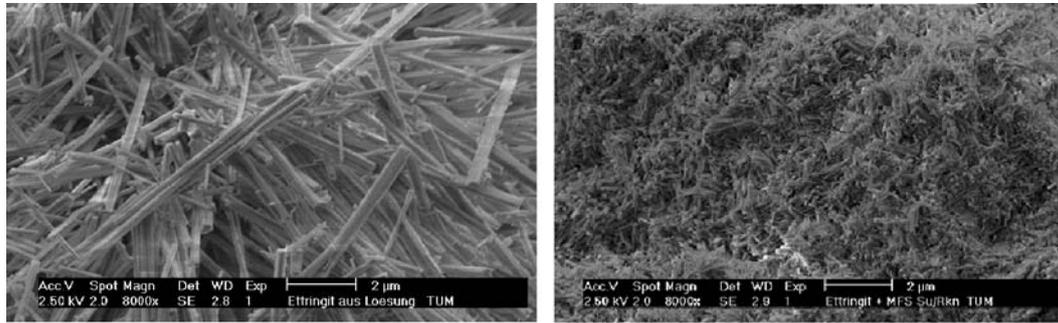
Fig. 3. ESEM micrograph of ettringite, prepared in the absence (left) and presence of PMS (right).

the stronger the adsorption. Therefore, PC-a showing high anionic character has much higher adsorption rate than PC-c.

The very different adsorption behaviour of polycondensate and polycarboxylate type superplasticizers on early hydration products helps to understand the different dosages of superplasticizer required for cements of diverse composition. In many cases, these were attributed to variations in aluminate content in the cements [20–26]. Obviously, the ettringite formed from the aluminate phase of the cement and $CaSO_4 \cdot nH_2O$ determines the dosage of superplasticizer to a great extent. Also, the rate of formation and the crystal size and shape (surface area) of ettringite will influence superplasticizer dosage. Monosulfate has less and all other early hydration phases show practically no effect on superplasticizer dosage. This underscores the importance of ettringite for cement–superplasticizer interaction.

Only for ettringite, a big difference between the adsorbed amount of polycondensate added at the beginning or at the end of the crystallization process was observed. Fig. 2 shows the adsorbed amounts for all superplasticizers for addition at the beginning and after completion of ettringite crystallization. As can be seen, the adsorbed amounts of polycondensates (PMS, BNS) are approx. 50% less when these superplasticizers are added at the end of the crystallization process. This effect might be explained by a decrease in zeta potential, specific surface area or rate of formation of ettringite during the crystallization process. Hence, when polycondensates are present during the crystallization process, higher amounts of superplasticizer are

required [27,28]. This result confirms the benefit of delayed addition known from practical use of polycondensates in concrete.

The adsorbed superplasticizers not only change the zeta potential, but also the size and morphology of the hydrate phases. Fig. 3 shows an environmental scanning electron micrograph (ESEM) of two different samples of ettringite. The first sample was precipitated in the absence of a superplasticizer, whereas the second one was prepared in the presence of PMS. In the presence of PMS, the ettringite crystals are much smaller. Also, the morphology changes from long and thin to short and compact needles. Similar effects were found also for BNS and polycarboxylate type superplasticizers. Most likely, the changes in size and morphology of the crystals induced by superplasticizers are either based upon a higher rate of nuclei formation or on preferred adsorption on specific crystal faces, thus preventing normal growth of the crystals. In contrast, crystal size and morphology of monosulfate and syngenite which show a very low zeta potential and do not adsorb any superplasticizer, were not changed in the presence of superplasticizers (see Fig. 4).

4. Conclusion

A positive zeta potential is necessary to achieve high superplasticizer adsorption. Among early cement hydration phases, ettringite and, to a less extent, monosulfate show positive zeta potentials. Therefore, they adsorb high amounts of superplasticizers. Syngenite, portlandite and gypsum show zero or negative zeta potentials and do not adsorb superplasticizers.
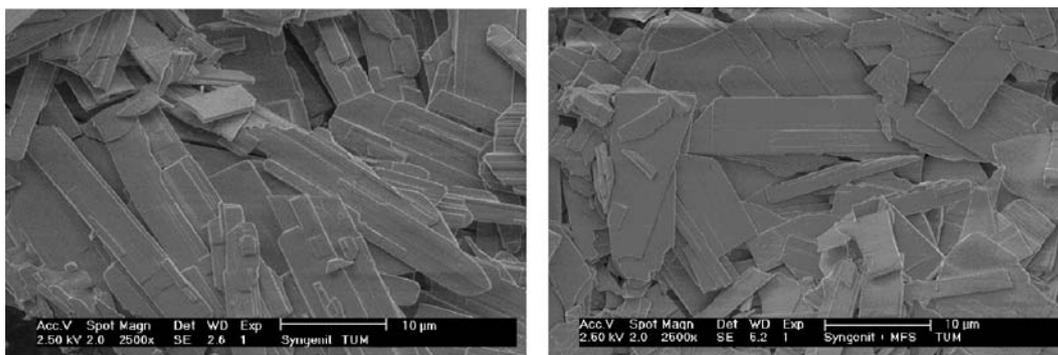

Fig. 4. ESEM micrograph of syngenite, prepared in the absence (left) and presence of PMS (right).
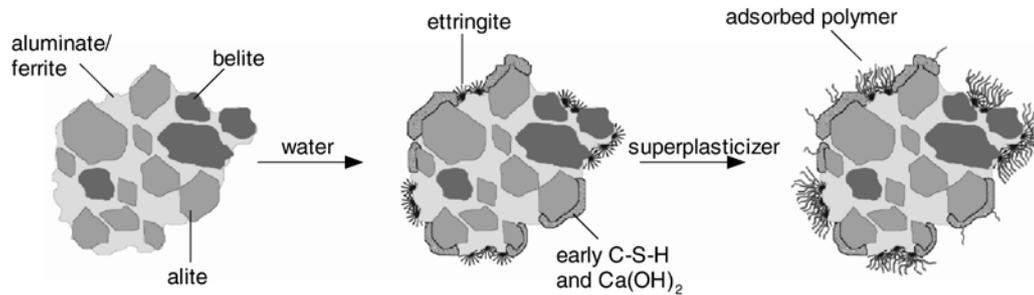
Fig. 5. Schematic representation of the cross section of a hydrating cement grain showing uneven polymer distribution on its surface.

Consequently, superplasticizers adsorbing on a hydrating cement grain are mainly concentrated on spots where ettringite crystallizes. The result is a mosaic structure for the hydrating cement grains with uneven distribution of polymer molecules on its surface. Fig. 5 gives a schematic representation of the formation of adsorbed polymer layer on a cement grain during its early hydration.

The absolute values of zeta potential for ettringite or any other mineral phase depend on the concentration of potential determining ions present in the pore solution. While these may vary with cement composition, w/c ratio, time of hydration etc., the same relative order of zeta potential values for different hydration phases and minerals present can be expected.

Zeta potential measurement of any cement or filler material (e.g. limestone, fly ash, slag etc.) allows to quickly determine its potential for admixture adsorption. Such results combined with data on specific surface area can provide a rough assessment of superplasticizer dosage required to disperse a given system. It also provides insight into cement–superplasticizer interaction.

References

[1] K. Yoshioka, E.-I. Tazawa, K. Kawai, T. Enohata, Adsorption characteristics of superplasticizers on cement component minerals, Cem. Concr. Res. 32 (2002) 1507–1513.

[2] L. Nachbaur, P.-C. Nkinamubanzi, A. Nonat, J.-C. Mutin, Electrokinetic properties which control the coagulation of silicate cement suspensions during early age hydration, J. Colloid Interface Sci. 202 (1998) 261–268.

[3] H. Viallis-Terrisse, A. Nonat, J.-C. Petit, Zeta-potential study of calcium silicate hydrates interacting with alkaline cations, J. Colloid Interface Sci. 244 (2001) 58–65.

[4] B. Jönsson, H. Wennerström, A. Nonat, B. Cabane, Onset of cohesion in cement paste, Langmuir 20 (2004) 6702–6709.

[5] M. Corradi, R. Khurana, R. Magarotto, Tailor-Made Superplasticizers for Modern Concrete, Eighth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Sorrento (Italy), SP 239-16, 2006, pp. 231–248.

[6] S. Diamond, L.J. Struble, Interaction between naphthalene sulfonate and silica fume in Portland cement pastes, Mater. Res. Soc. Symp. Proc. 114 (1988) 117–126.

[7] D. Atarashi, E. Sakai, M. Daimon, Interaction between superplasticizers and clay minerals, Semento, Konkurito Roubunshu 58 (2004) 387–392.

[8] T. Nawa, H. Ichiboji, M. Kinoshita, Influence of temperature on fluidity of cement paste containing superplasticizer with polyethylene oxide graft chains, Sixth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Nice (France), SP 195-13, 2000, pp. 195–210.

[9] E.E. Hekal, E.A. Kishar, Effect of sodium salt of naphthalene–formaldehyde polycondensate on ettringite formation, Cem. Concr. Res. 29 (1999) 1535–1540.

[10] Y. Kerui, Z. Caiwen, L. Zhigang, The influence of calcium lignosulphonate–sodium bicarbonate on the status of ettringite crystallization in fly ash cement paste, Cem. Concr. Res. 32 (2002) 51–56.

[11] W. Prince, M. Edwards-Lajnef, P.-C. Aitcin, Interaction between ettringite and a polynaphthalene sulfonate superplasticizer in a cementitious paste, Cem. Concr. Res. 32 (2002) 79–85.

[12] V. Fernon, A. Vichot, N. Le Goanvic, P. Colombet, F. Corazza, U. Costa, Interaction between Portland cement hydrates and polynaphthalene sulfonates, Fifth CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, Rome (Italy), SP-173-12, 1997, pp. 225–248.

[13] J. Plank, Z. Dai, N. Zouaoui, D. Vlad, Intercalation of Polycarboxylate Superplasticizers into C_3A Hydrate Phases, in: V.M. Malhotra (Ed.), Eighth CANMET/ACI Conference on Superplasticizers in Concrete, ACI, Sorrento, SP-239-14, 2006, pp. 201–214.

[14] J. Plank, Z. Dai, P. Andres, Preparation and characterisation of new Ca–Al–polycarboxylate layered double hydroxides, Mater. Lett. 60 (2006) 3614–3617.

[15] J. Plank, H. Keller, P.R. Andres, Z. Dai, Novel organo-mineral phases obtained by intercalation of maleic anhydride–allyl ether copolymers into layered calcium aluminium hydrates, Inorg. Chim. Acta 359 (2006) 4901–4908.

[16] J. Plank, D. Vlad, A. Brandl, P. Chatziagorastou, Colloidal chemistry examination of the steric effect of polycarboxylate superplasticizers, Cem. Int. 3 (2005) 100–110.

[17] L.J. Struble, Synthesis and Characterization of Ettringite and Related Phases, 8th Int. Conf. Chem. Cem., Rio de Janeiro, 1986, pp. 582–588.

[18] A.S. Dukhin, P.J. Goetz, Acoustic and electroacoustic spectroscopy for characterizing concentrated dispersions and emulsions, Adv. Colloid Interface Sci. 92 (2001) 73–132.

[19] A.S. Dukhin, P.J. Goetz, Ultrasound for Characterizing Colloids: Particle Sizing, Zeta Potential, Rheology, Elsevier Science B. V., Amsterdam, 2002.

[20] S. Chandra, J. Björnström, Influence of superplasticizer type and dosage on the slump loss of Portland cement mortars — Part I, Cem. Concr. Res. 32 (2002) 1605–1611.

[21] E. Sakai, K. Yamada, A. Ohta, Molecular structure and dispersion–adsorption mechanisms of comb-type superplasticizers used in Japan, J. Adv. Concr. Technol. 1 (2003) 16–25.

[22] P.-C. Nkinamubanzi, B.-G. Kim, P.-C. Aitcin, Some key cement factors that control the compatibility between naphthalene-based superplasticizers and ordinary Portland cements, Sixth CANMET/ACI International Conference on Superplasticizers and other Chemical Admixtures in Concrete, Nice (France), Supplementary Papers, 2000, pp. 33–54.

[23] P.-C. Aitcin, C. Jolicoeur, J.G. MacGregor, Superplasticizers: how they work and why they occasionally don't, Concr. Int. (1994) 45–52.

[24] K. Yamada, S. Ogawa, S. Hanehara, Working mechanism of poly-beta-naphthalene sulfonate and polycarboxylate superplasticizer types from point of cement paste characteristics, Sixth CANMET/ACI International Conference on Superplasticizers and other Chemical Admixtures in Concrete, Nice (France), SP 195-23, 2000, pp. 367–382.

[25] H. Uchikawa, D. Sawaki, S. Hanehara, Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement paste, Cem. Concr. Res. 25 (1995) 353–364.

[26] M.Y.A. Mollah, W.J. Adams, R. Schennach, D.L. Cocke, A review of cement–superplasticizer interactions and their models, Adv. Cem. Res. 12 (2000) 153–161.

[27] R.J. Flatt, Y.F. Houst, A simplified view on chemical effects perturbing the action of superplasticizers, Cem. Concr. Res. 31 (2001) 1169–1176.

[28] W. Prince, M. Espagne, P.-C. Aitcin, Ettringite formation: a crucial step in cement superplasticizer compatibility, Cem. Concr. Res. 33 (2003) 635–641.