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Study of the influence of superplasticizers on the hydration of cement paste using nuclear magnetic resonance and X-ray diffraction techniques

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Abstract

Melamine and naphthalene-based superplasticizers have been used, over the past few decades, in order to improve the workability of concrete. Recently, more efficient copolymer formulations have been introduced for the same purpose. However, the influence of these chemical admixtures on the microstructure of the hardened concrete and, consequently, on its properties still needs to be extensively evaluated. Accordingly, the present work analyzes the hydration characteristics of cement pastes with naphthalene, melamine and copolymer-based superplasticizers, using the techniques of X-ray diffraction (XRD) and nuclear magnetic resonance (NMR), up to the age of 28 days. The results indicate a significant influence of the superplasticizer on the growth rates of the hydrates and on the state of polymerization of the silicates. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Admixture; Hydration products; Cement paste; X-ray diffraction; Nuclear magnetic resonance

1. Introduction

Superplasticizers are incorporated in concrete mainly to modify its properties in the fresh state, and more specifically to yield high workability at low water/cement ratios. Subsequently, after the setting of the cement, the superplasticizer is not expected to affect the properties of the concrete significantly. Nevertheless, the influence of the superplasticizer on the characteristics of the hardening and hardened concrete is largely unclear. A better understanding of these aspects is, therefore, essential for further improvement of these admixtures and for analyzing the long-term properties of the concrete. Along these lines, the influence of the incorporation of the superplasticizer on cement paste, and more precisely, on its hydration processes, is studied in the present work.

The present study deals with the analysis of cement pastes using ^{29}Si nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) techniques. The complementary use of these approaches can be expected to provide a more complete picture of the hydration processes with respect to the consumption of the crystalline anhydrous phases of the cement during hydration, as well as the formation of the crystalline hydrates and the amorphous C–S–H.

Four superplasticizers have been used and the observations were made on the superplasticized pastes, along with a reference paste, at several ages: 15 min after mixing, during setting and at the ages of 2, 7, 14 and 28 days. The pastes incorporated the maximum superplasticizer dosage, defined in terms of the saturation dosage determined in the Marsh cone test.

2. Materials used

Cement of type CEM I 52.5 R (as in European Standard ENV 197-1:92), with the composition and properties shown in Table 1, was used in the study, along with four commercially available superplasticizers, designated as SN, SM, SC and SMN (see Table 2). The superplasticizer dosages are specified in this study as the solid superplasticizer/cement

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Table 1
Properties of the cement used

Chemical composition (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI[a]	Cl^-
20.18	5.47	3.48	63.05	1.81	3.25	0.15	0.86	1.76	0.01

Mineralogical composition (%)

C_3S	C_2S	C_3A	C_4AF	Na_2O equivalent
52.33	18.38	8.6	10.59	0.71

Physical properties

Blaine fineness (cm^2/g)	Specific gravity (kg/m^3)	Initial setting time (min)	Final setting time (min)
4250	3150	100	150

[a] Loss on ignition.

ratios (sp/c), by weight, and the water contained in the superplasticizer is taken into account in the water/cement ratio (w/c), which was maintained as 0.33. The pastes are labeled according to the superplasticizer that they contain. Along with these cement paste systems, a reference paste, without any superplasticizer, was also characterized.

The dosage of each superplasticizer was obtained as the saturation point in the Marsh cone test [1,2]. The apparatus consists of an inverted hollow metal cone with an opening of 8 mm at the bottom. A fixed volume of paste (800 ml) is poured into the cone and the time taken for 200 ml to flow through it is determined. Tests are performed on pastes with increasing superplasticizer dosage, and the flow times are plotted with respect to sp/c. The plots reflect the decrease in flow time (or the increase in fluidity) until the saturation dosage, beyond which the flow time does not change significantly. Accordingly, the saturation dosage of the superplasticizer has been chosen for each of the pastes studied in order to compare their behaviors at the maximum fluidity.

The pastes were mixed in a 5-liter Hobart-type blender with two velocities, 120 rpm (high) and 60 rpm (low). The following mixing sequence was used: the cement was mixed with a fixed quantity of water (corresponding to w/c = 0.245) at low speed for 2 min; then, the superplasticizer and the remaining water were added and mixed for 0.5 min at low speed and for 2.5 more minutes at high speed. Fig. 1 gives the curves obtained for all the cement paste systems showing the evolution of the Marsh cone flow time as a function of the superplasticizer dosage. The corresponding saturation superplasticizer dosages in the pastes SN, SM, SC and SMN are sp/c = 1%, 1.5%, 0.3% and 1%, respectively.

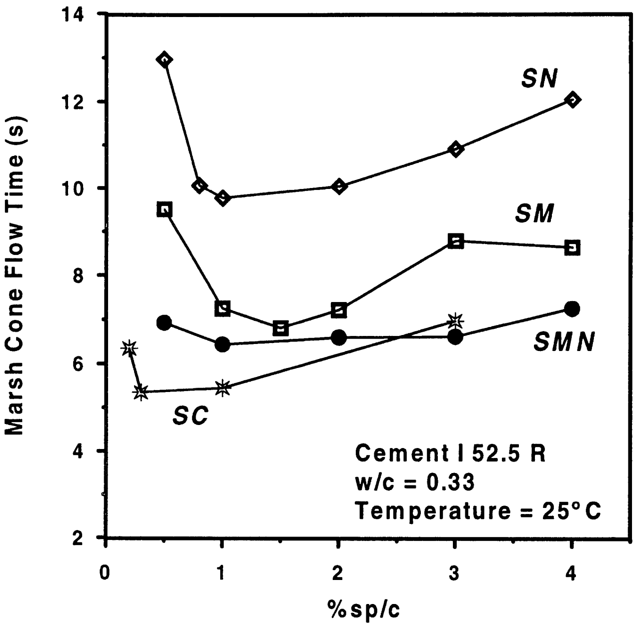

Fig. 1. Determination of the saturation dosage for SN, SM, SC and SMN pastes.

Samples of each paste were taken at the ages of 15 min, 2, 7, 14 and 28 days. In addition, another sample was taken during setting, at the age denoted here as the half-setting time, which corresponds to a Vicat penetration [3] reading of 20 mm, using a needle with a diameter of 1.13 mm and a weight of 300 g, at a temperature of 20 °C. The half-setting times for the reference paste and the superplasticized pastes SN, SM, SC and SMN are 160, 480, 460, 730 and 500 min, respectively. Note that the half-setting times clearly reflect the retarding effect of the superplasticizer on the setting of the cement, with the superplasticizer SC leading to more retardation than the others.

For the analyses, the samples were ground in an agate mortar and immersed in acetone during 45 s, rinsed twice in ethanol and then maintained in the same, with the aim of preventing further hydration, by removing the evaporable water. Just before each analysis, the samples were dried in an oven at 60 °C.

Table 2
Characteristics of the superplasticizers used

Designation	SN	SM	SC	SMN
Type	Naphthalene sulfonic acid based	Melamine sulfonic acid based	Polycarboxylic acid based	Melamine–naphthalene based blend
Density (g/cm^3)	1.18	1.25	1.08	1.20
Solid content (%)	35	40	31	39.5
Range of dosage recommended by supplier (by weight of cement)	0.18–0.7%	0.6–1.2%	0.1–0.3%	data unavailable

3. ^{29}Si NMR

^{29}Si magic angle spinning (MAS) NMR spectroscopy is a technique used to characterize the state of polymerization of the silicates (i.e., tetrahedral SiO_4^{4-}) in the cement paste [4]. The individual tetrahedrons (called monomers and designated as Q^0) of the anhydrous silicate phases of the cement (i.e., C_3S, C_2S) are transformed due to hydration into C–S–H gel, through silicate polymerization. In this process, the tetrahedrons connect through their oxygen atoms giving rise to polymeric states, known as dimers (Q^1) and polymeric chains (Q^2). Each of these states reflects the degree of polymerization of the silicates in the paste, and is identified by a peak in the NMR spectrum, when plotted as a function of the chemical shift, which represents the relative shift with respect to the frequency of absorption of the ^{29}Si (i.e., 59.63 MHz).

Here, a Bruker AMX 300 MHz solid-state high-resolution spectrometer with thick-wall zirconia rotors, rotating at 3800 Hz, was used to carry out the ^{29}Si MAS NMR analysis of the pastes. Tests were performed on pastes at the half-setting time, 2, 7 and 28 days.

Fig. 2 shows the ^{29}Si NMR spectra of the reference cement paste along with those of the superplasticized pastes SN, SM, SC and SMN. Two peaks can be identified in each of the plots corresponding to Q^0, in the chemical shift range of -66 to -74 ppm, and Q^1, in the range of -75 to -82 ppm, respectively. The plots show that the amount of dimers gradually increases during the first 28 days, with a reduction of the monomeric silicate. Note that no Q^2 was detected in the spectra.

Since the peaks in the NMR spectra overlap, a semi-quantitative method is used to analyze the curves obtained at different ages. The areas of the Q^0 and Q^1 peaks for each spectrum, denoted respectively as A_0 and A_1, are separated by drawing a vertical line through the valley, as in Fig. 3. The relative area of the Q^1 peak (A_1/A_0) obtained for each paste is given in Table 3. It can be observed that the superplasticizer has some effect on the polymerization of the silicates during the hydration process. Its incorporation appears to lead to the formation of a lower amount of dimers (i.e., Q^1) beyond the age of 2 days, reflected by lower A_1/A_0 areas in all the superplasticized pastes, when compared with the reference paste. For example, at 28 days, the degree of polymerization in the pastes SN, SM, SC and SMN, as represented by the A_1/A_0 area, is 19%, 21%, 11% and 12% lower than in the reference paste, respectively.

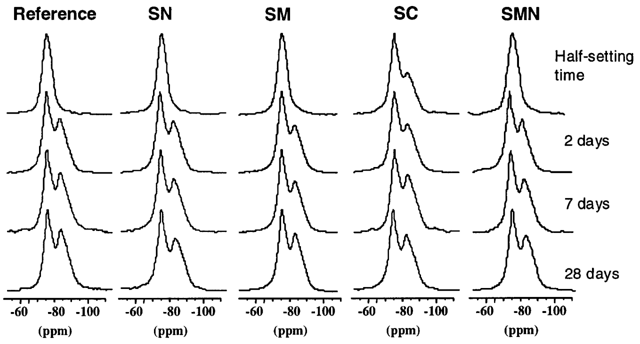

Fig. 2. ^{29}Si MAS NMR spectra of reference, SN, SM, SC and SMN pastes at half-setting time, 2, 7 and 28 days.

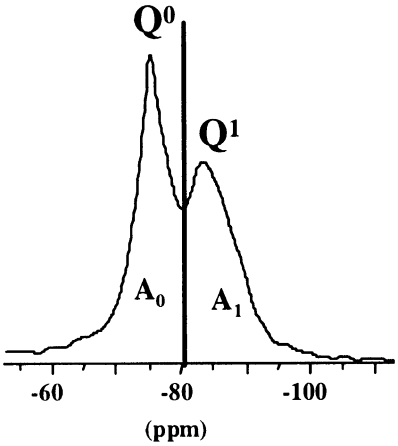

Fig. 3. Integration method for analyzing the ^{29}Si MAS NMR spectra.

On the other hand, in the SC paste, the formation of dimers can be detected during the setting process itself. Also, the SC paste shows the highest increase of the relative area of Q^1 between 2 and 7 days, indicating a higher rate of formation of C–S–H.

4. XRD

XRD is used to identify the polycrystalline phases of cement and hardened cement paste through the recognition of the X-ray patterns that are unique for each of the crystalline phases [5]. Consequently, this technique allows the detection of ettringite (AF_t), monosulfate (AF_m) and portlandite (CH) and the consumption of the anhydrous phases of the cement (i.e., gypsum, C_3S, C_2S, C_3A and C_4AF), as well as the formation of amorphous C–S–H, which is indicated by an upward shift of the diffractogram.

The qualitative XRD analyses were performed in a Siemens D-500 X-Ray Powder Diffractometer with a scintillation counter and graphite secondary monochromator. In this apparatus, the $K_\alpha Cu$ ($\lambda = 1.5418$ Å) radiation is generated in a Cu tube at 30 mA and 40 kV. The tests were performed over a Bragg angle (2θ) range of 4–70°, using an angular

Table 3
Relative area A_1/A_0 at different ages

	Paste				
Age of the paste	Reference	SN	SM	SC	SMN
Half-setting time	0	0	0	0.52	0
2 days	0.80	0.72	0.63	0.68	0.69
7 days	0.98	0.75	0.69	0.87	0.83
28 days	0.99	0.80	0.78	0.88	0.87

Table 4
Relative evolution of the crystalline phases with age

	Age	C_3S, C_2S	C_3A	C_4AF	Gypsum	Ettringite	Portlandite
Reference	15 min	P	P	P	P	A	A
	Half-setting	P	P	P	P↓	P	A
	2 days	P↓↓	P↓	P↓	A	P	P
	7 days	P↓	P	P	A	P	P↑
	14 days	P	P↓↓	P	A	P	P
	28 days	P↓	A	P↓	A	P	P
SN	15 min	P	P	P	P	T	A
	Half-setting	P↓	P↓↓	P	P	T	A
	2 days	P↓	P	P	T	P↑	P
	7 days	P	P	P	A	P↑	P
	14 days	P	P	P↓	A	P↓	P
	28 days	P↓↓	A	P↓	A	P↑	P↑
SM	Half-setting	P	P	P	T	T	A
	2 days	P↓	P	P	T	P↑	P
	7 days	P↓↓	P↓	P↓	A	P↑	P
	14 days	P↓	P↓↓	P	A	P↓	P
	28 days	P↓	T	P↓	A	P↓	P
SC	15 min	P	P	P	P	T	A
	Half-setting	P↓	P	P	P↓	P	P
	2 days	P↓↓	P	P	A	P	P↑↑
	7 days	P↓	P	P	A	P↑	P↑↑
	14 days	P↓	P	P	A	P	P
	28 days	P↓	T	P↓↓	A	P	P↑
SMN	15 min	P	P	P	P	T	A
	Half-setting	P↓	P↓	P	P↓↓	T	A
	2 days	P↓↓	T	P↓	A	P	P
	7 days	P↓	T	P	A	P↓	P
	14 days	P↓	A	P↓	A	P↑	P
	28 days	P↓	A	P	A	P↓	P

↑↓ Increase or decrease of the phase, respectively, with reference to the previous age.
Abbreviations: P, present; A, absent; T, traces.

velocity of 0.05° per 3 s on the samples corresponding to the ages of 15 min, half-setting time, 2, 7, 14 and 28 days.

The relative evolution, with age, of the crystalline phases identified in the diffractograms of the different pastes is summarized in Table 4. The principal components of the anhydrous cement (i.e., C_3S, C_2S, C_3A and C_4AF) have been identified at all the ages studied. Ettringite was detected at the half-setting time since it forms immediately after the mixing of water and cement, while portlandite is detected in samples that are older than 2 days. In the case of the C_2S phase, the peaks of maximum intensity overlap with those of C_3S, making the determination of its evolution difficult. Therefore, their trends are reported jointly in the table. Gypsum is detected during setting but after two days the sulfates are mainly in the form of ettringite.

The results show some qualitative differences in the hydration rate due to the incorporation of superplasticizers. In the SC paste, the formation of portlandite can be detected at the half-setting time, as seen in Fig. 4, while in the other pastes, portlandite was not observed until the age of 2 days. The rate of formation of portlandite in the SC paste is also higher between 2 and 7 days, indicating faster growth of the C–S–H phase.

The incorporation of superplasticizer also leads to a higher rate of the primary growth of ettringite, as shown by the results obtained at the age of 15 min. On the other hand, in the reference paste, no primary growth of ettringite was detected by XRD. Another difference that can be observed in the table is a faster secondary formation of ettringite in the SN and SM pastes, at least up to 7 days. With regards to the consumption of gypsum, it can be observed that the incorporation of superplasticizer SM leads to the fastest decrease in the gypsum content. Also, a decrease in AF_t can be observed in the SN, SMN and SM pastes between 7 and 14 days. Though this is related to the formation of the monosulfate (AF_m), none of it was detected in any of the pastes studied, up to 28 days, probably due to its presence in very small quantities [6].

5. Discussion

The incorporation of a superplasticizer in cement paste clearly affects the rate of formation of the hydrates, both the amorphous C–S–H and the crystalline phases, as seen in the results of the NMR and XRD analyses.

In the NMR study, a lower polymerization of the silicates has been observed in the presence of the superplasticizer, which is reflected by a lower proportion of dimers (Q^1) at the ages of 2–28 days. Yousuf et al. [7]

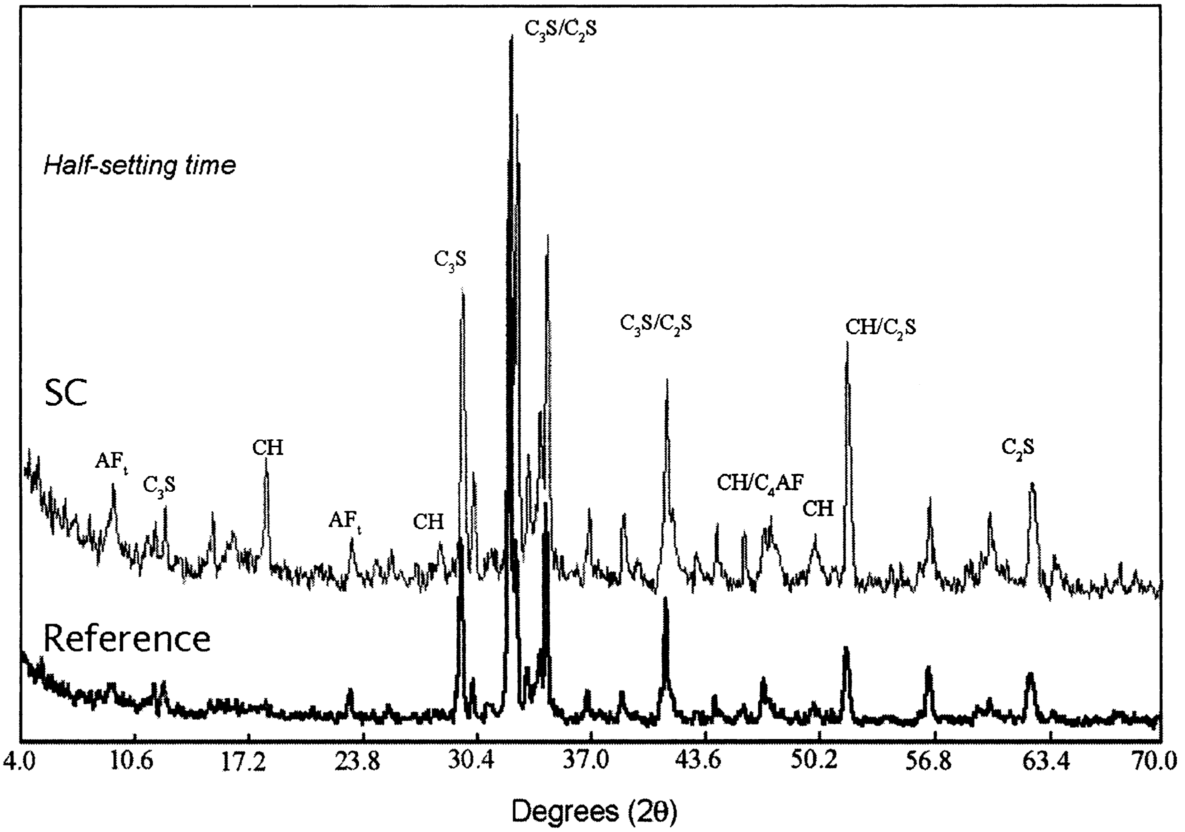

Fig. 4. XRD plots of the reference and SC pastes at the half-setting time.

reported similar trends with a lignosulfonate plasticizer. Since the formation of dimers is indicative of the formation of C–S–H gel, the lower proportion of dimers implies lesser C–S–H formation, at early ages, when a superplasticizer is incorporated. This is in accordance with the conclusion of Legrand and Wirquin [8] that the incorporation of the superplasticizer leads to lower amount of hydrates for the same strengths, due to a better dispersion of the cement particles.

Interestingly, the beginning of dimer formation in the SC paste was detected during setting (i.e., at the half-setting time). This implies an accelerated formation of C–S–H that is confirmed by the early formation of portlandite detected in the XRD analysis. Though all the pastes had the same penetration resistance (i.e., 20 mm in the Vicat apparatus) at half-setting time, the degree of hydration can vary from one paste to another; for example, the accelerated formation of C–S–H was detected only in the SC paste. This seems to confirm the absence of a direct relationship between the setting process, as measured through Vicat penetration, and the state of hydration [9].

With regards to the formation of ettringite in the early stages of hydration, the XRD analysis indicates the influence of the superplasticizer as early as the age of 15 min, when AF_t is detected in the superplasticized pastes. Also, more rapid growth of ettringite can be observed in the SN and SM pastes up to 7 days. The influence of the superplasticizer on ettringite formation may reflect its effect on the equilibrium between sulfates and C_3A in the pore solution as proposed by previous researchers [10–13].

6. Conclusions

The combined use of NMR and XRD is helpful in evaluating the hydration products, more than the individual use of any of the methods. The NMR technique allows the study of the state of polymerization of the silicates while the XRD analysis characterizes the crystalline anhydrous phases and hydrates. In the context of the materials and variables studied in the present work, the following conclusions can be drawn from the results obtained:

- The incorporation of superplasticizer in cement paste clearly influences the hydration process, especially the growth rate of the hydrates.
- The formation of C–S–H gel is affected by the superplasticizer, causing a lower amount of polymerized silicates, which is indicative of lower C–S–H gel formation.
- The formation of C–S–H is initiated earlier in the SC paste as demonstrated by the detection of silicate polymerization during the setting process in the NMR analysis and the detection of portlandite in the XRD analysis.

- The incorporation of the superplasticizer clearly alters the growth rate of ettringite. At the age of 15 min, no AF_t was detected in the XRD analysis of the reference paste whereas it was observed in all the superplasticized pastes, implying the accelerated formation of this phase. Also, secondary growth of ettringite is more evident in pastes with superplasticizer, especially in the SN and SM pastes.

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References

[1] F. de Larrard, A method for proportioning high-strength concrete mixtures, Cem. Concr. Aggregates (ASTM) 12 (2) (1990) 47–52.

[2] L. Agulló, B. Toralles-Carbonari, R. Gettu, A. Aguado, Fluidity of cement pastes with mineral admixtures and superplasticizer. A study based on the Marsh cone test, Mater. Struct. 32 (1999) 479–485.

[3] EN 196-3, Methods of testing cement: determination of setting time and soundness, European standard, CEN, Brussels, 1987.

[4] H. Zanni, R. Rassem-Bertolo, L. Fernandez, S. Masse, P. Nieto, La résonance magnétique nucléaire: Une technique pour l'étude des ciments, Bull. Lab. Ponts Chaussées 195 (1995) 61–72.

[5] Powder Diffraction File Search Manual, Joint Committee on Powder Diffraction Standards (JCPDS), International Center for Diffraction Data, Swarthmore, PA, USA, 1980.

[6] H.F.W. Taylor, Cement Chemistry, Thomas Telford Publ., London, 1997.

[7] M. Yousuf, A. Mollah, P. Palta, T.R. Hess, R.K. Vempati, D.L. Cocke, Chemical and physical effects of sodium lignosulfonate superplasticizer on the hydration of Portland cement and solidification/stabilization consequences, Cem. Concr. Res. 25 (3) (1995) 671–682.

[8] C. Legrand, E. Wirquin, Study of the strength of very young concrete as a function of the amount of hydrates formed. Influence of superplasticizer, Mater. Struct. 27 (1994) 106–109.

[9] S.P. Jiang, J.C. Mutin, A. Nonat, Studies on mechanism and physicochemical parameters at the origin of the cement setting: I. The fundamental processes involved during the cement setting, Cem. Concr. Res. 25 (4) (1995) 779–789.

[10] L.M. Meyer, W.F. Perenchio, Theory of concrete slump loss as related to the use of chemical admixtures, Concr. Int. 1 (1) (1979) 36–43.

[11] S.M. Khalil, M.A. Ward, Effect of sulphate content of cement upon heat evolution and slump loss of concretes containing high-range water-reducers (superplasticizers), Mag. Concr. Res. 32 (110) (1980) 28–38.

[12] F. Basile, S. Biagini, G. Ferrari, M. Collepardi, Effect of the gypsum state in industrial cements on the action of superplasticizers, Cem. Concr. Res. 17 (5) (1987) 715–722.

[13] E. Hanna, K. Luke, D. Perraton, P.C. Aïtcin, Rheological behavior of Portland cement in the presence of superplasticizer, in: V.M. Malhotra (Ed.). Proc. Third Intnl. Conf. on Superplasticizers and Other Chemical Admixtures in Concrete (Ottawa, Canada), ACI SP-119. American Concrete Institute, DE, USA, 1989, pp. 171–188.