論文 Study on Cement-Superplasticizer Compatibility and its Effect on Rheology and Filtration Properties of High-performance Cement Grout

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ABSTRACT: The objective of this study is to highlight the effect of cement-superplasticizer compatibility on rheology and filtration properties of high-performance portland cement grout. Two different types of superplasticizer, a β-naphthalene sulfonate and a polycarboxylic were used in combination with three cements, corresponding to ordinary, low heat and belite cements. The investigated mixtures were prepared using a W/C ranging between 0.30 and 0.36. Test results showed that the rheological behavior and filtration properties of cement grout are mainly affected by the cement-superplasticizer combination.

KEYWORDS: Cement, superplasticizer, compatibility, rheology, filtration, cement grout

1. INTRODUCTION

Suitable fresh properties of cement-based systems may be achieved by a proper selection of cement-superplasticizer combination. Indeed, compatible combination can achieve high initial fluidity as well as good fluidity retention. Various studies were therefore carried out to identify relevant parameters controlling the cement-superplasticizer compatibility from the chemistry point of view. Actually, it is broadly acknowledged that the dispersing ability of naphthalene-based superplasticizer (PNS) types decreases when dealing with low alkali-sulfate cement [1,2]. On the other hand, the dispersing efficiency of the polycarboxylic type is reduced by the sulfate ions content [1].

Although considerable advances have been achieved in elucidating the relevant parameters affecting the compatibility between cement and superplasticizer, there is little information regarding the effect of compatibility/incompatibility on rheology and filtration properties of high-performance cement grouts, such as those used for filling post-tensioning ducts. The main objective of this investigation is to highlight the effect of cement-superplasticizer compatibility on rheology and filtration properties of high-performance cement-based grout. The knowledge of rheological behavior is important to predict and evaluate the ease of pumping and flowing. On the other hand, filtration properties are of special interest for quality control of fresh grout during pumping.

2. EXPERIMENTAL PROGRAM

2.1 MATERIAL PROPERTIES AND TEST PROCEDURES

Three Japanese commercial portland cements corresponding to normal (NO), low heat (LH), and belite (BC) cements were used. Table 1 presents the component composition of these cements. A polycarboxylic (PC) and a β-naphthalene sulfonate (PNS) were used for the superplasticizer and were supplied in powder form. The grout mixtures were prepared in batches of 4 L and mixed with a mixer rotating at 1000 rpm. The batching sequence consisted in mixing the water and

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superplasticizer for 30 seconds. The cement was then introduced gradually over 1 minute and the grout was mixed for a total time of 8 minutes.

Table 1. Component composition of the cements

Type	C_3S	C_2S	C_3A	C_4AF	Blaine (cm^2/g)
NO	60.5	14.1	7.0	8.8	3310
LH	24.0	56.0	3.0	10.0	3470
BC	34.0	47.0	3.0	8.0	4150

The fluidity was determined using a mini-slump test. The mini slump test consists in a cylindrical mold having an internal diameter of 40 mm and a height of 40 mm. The reported mini-slump value corresponds to the average of two perpendicular measurements. Rheological measurements were performed with a coaxial viscometer with 1.5-mm gap size. The test parameters, such as the time duration of testing and the maximum shear rate, were optimized to reduce the risk of slip and sedimentation during measurements. Flow curves were obtained by first increasing (ascendant) and then decreasing (descendant) the shear rate from 5 to 240 s^{-1} during two minutes. The viscometer was calibrated using JS500 standard solution complying with JIS Z 8809 specifications before carrying measurements on paste. Fluidity and rheological measurements were assessed immediately after mixing, corresponding to 8 min, 30, 60, and 90 min of age.

Filtration properties, or the removal of water under pressure (forced bleeding), of grouts were determined using a cylindrical filter vessel. A sample of 300-mL was poured inside the vessel and subjected to a constant air-pressure maintained between 0.50 and 0.55 MPa applied from the top of the vessel. Bleed water filtrated through the grout pack and the filter paper placed at the bottom of the vessel during 10 minutes were collected. The bleed water was expressed as the percentage of the mixing water contained in 300-mL sample.

2.2 MIXTURE PROPORTIONING

For a given W/C and superplasticizer-cement couple, the optimum dosages of superplasticizer that can achieve stable grouts (no-bleeding) with the highest mini-slump spread possible are determined. Table 2 summarizes the optimum dosages of each superplasticizer type given the type of cement and the W/C. Given the efficiency of each type of superplasticizer, the mini-slump spread of mixtures made with PC type is maintained between 190 and 205 mm. On the other hand, the mini-slump for those made with PNS type is ranging between 140 and 160 mm. It must be mentioned however that the mini slump obtained with BC-PNS couple and a W/C of 30% was limited to 130 mm.

Table 2. Optimum dosages of superplasticizer for different W/C and types of cement

Cement	Normal Cement (NO)		Low Heat Cement (LH)		Belite Cement (BC)	
SP type	PNS (%)*	PC (%)*	PNS (%)*	PC (%)*	PNS (%)*	PC (%)*
W/C = 30%	0.40	0.20	0.45	0.14	0.45	0.12
W/C = 33%	0.40	0.16	0.45	0.12	0.45	0.10
W/C = 36%	0.35	0.12	0.35	0.08	0.35	0.08

*: Percentage of superplasticizer per mass of cement

3. TEST RESULTS AND DISCUSSION

3.1 CEMENT-SUPERPLASTICIZER COMPATIBILITY IN TERMS OF INITIAL FLUIDITY AND FLUIDITY RETENTION

The effect of cement-superplasticizer combination on the initial mini-slump spread and its variation with age for mixtures made with 30% W/C is shown in Fig. 1. Although, the dosage of PC is just half or lower than half of that of PNS, it can be observed that mixtures incorporating PC type show higher fluidity than those made with PNS, regardless of the W/C. Furthermore, when using the PC type, the fluidity retention is higher than that obtained with the PNS, especially for NO and LH cement types. Indeed, in case of mixtures incorporating PNS type, a considerable loss of fluidity is observed, especially for LH and BC cements. It must be noted that the same tendency is observed with 33 and 36% W/C mixtures, except that better fluidity retention is obtained with NO-PNS couple. Contrarily to the result observed in this study, it was reported that 30% W/C paste made with BC-PC combination exhibited good fluidity retention [1], and the loss of fluidity observed in this case is mainly due to the low dosage of PC used (0.12%) compared to 0.20% used in reference 1. The low mini-slump and loss of fluidity observed with mixtures made with LH-PNS and BC-PNS combinations, regardless of the W/C, is usually described as an incompatibility phenomena [1,2].

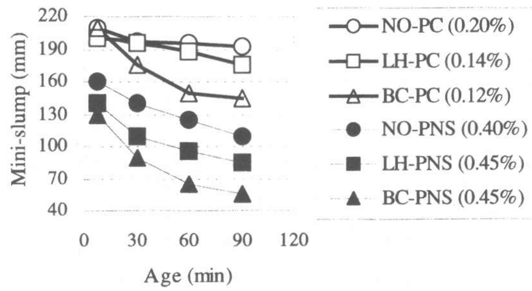

Fig. 1. Variation of the mini slump (W/C = 30%)

3.2 EFFECT OF CEMENT-SUPERPLASTICIZER COMBINATION ON RHEOLOGICAL BEHAVIOR OF GROUT

The flow curves have been modeled using the Hershel-Bulkely model ($\tau = \tau_y + k\gamma^n$), where τ is the shear stress (Pa), τ_0 is the yield stress (Pa), k is the consistency (Pa.s^n), γ is the shear rate (s^{-1}), and n is the power index. The exponent (n) describes the degree of pseudo-plasticity of grout. a) Shear thinning if $n < 1$, **b)** Shear thickening if $n > 1$, and **c)** a true plastic Bingham model when $n = 1$, where k is the plastic viscosity.

Figure 2 shows the flow curve for 30% W/C mixtures made with NO cement and different superplasticizer type. It can be state that in terms of pseudo-plasticity behavior, mixtures containing PC type exhibited higher degree of shear thickening (higher n) than those made with PNS. However, mixtures made with PNS showed higher consistency (k) values. A proper interpretation of the power index (n) may be obtained through a numerical relation between Log (shear stress)-Log (shear rate), where n represents clearly the slope of the line.

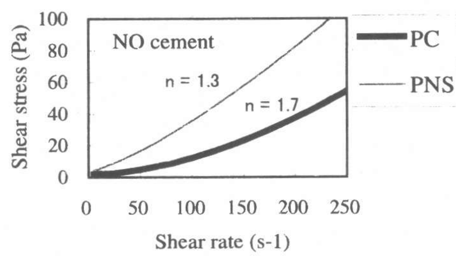

Fig. 2 Flow curve for 30% W/C mixtures

Figure 3 shows the flow curves for 30% W/C mixtures made with PC and PNS types. Mixtures incorporating PC type and proportioned with a W/C of 30% exhibited a shear thickening behavior, regardless of the type of cement. However, for those containing PNS type, NO and BC exhibited again a shear thickening behavior, but LH cement showed a shear thinning behavior. It must be noted that for a given type of superplasticizer, NO cement exhibited the highest degree of shear thickening, regardless of the W/C.

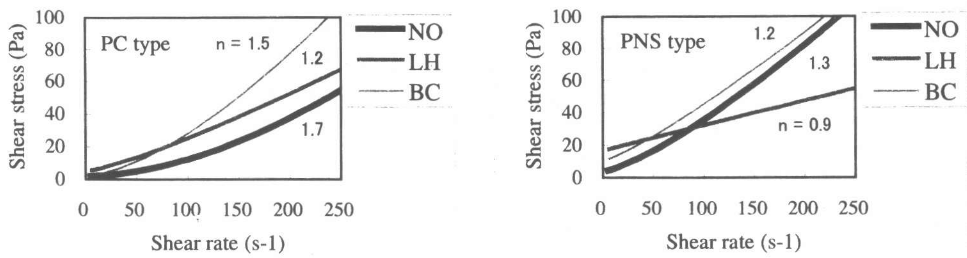

Fig. 3 Flow curve for 30% W/C mixtures

As can be observed in Fig. 4, the increase in W/C resulted in lowering the degree of pseudo-plasticity for all combinations. For a W/C of 33%, LH cement exhibited a shear thinning behavior, regardless of the type of superplasticizer. However, the shear thickening behavior observed with NO and BC is persistent. The increase in W/C from 33 to 36% resulted again in a shear thinning behavior for grouts made with LH cement and a shear thickening for those made with NO and BC cements. It can be stated, therefore, that in general the combination of NO and BC cement with PC or PNS types resulted in a shear thickening behavior, regardless of the W/C. On the other hand, the combination of LH cement with PC resulted in shear thickening at low W/C of 30% and a shear thinning when using higher W/C of 33 and 36%. However, the use of LH cement in combination with PNS resulted in a shear thinning behavior, regardless of the W/C. Since both LH and BC cements are known to be incompatible with PNS type and since LH-PNS exhibited a shear thinning behavior while BC exhibited a shear thickening behavior with PNS and PC, it can be stated that the shear thickening behavior is probably a physical phenomena due to the

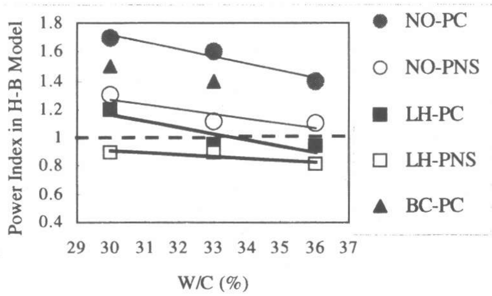

Fig. 4 Effect of W/C on the power index

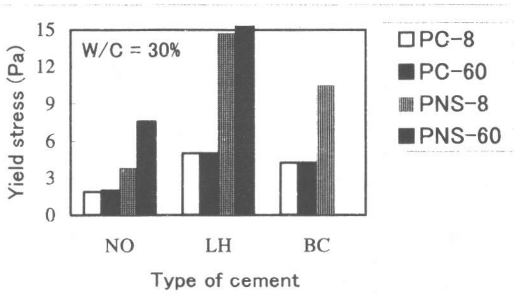

Fig. 5 Effect of type of cement on yield stress

dispersion mechanism of each type of superplasticizer and its affinity with cement particles.

In terms of the yield stress, it can be observed on Fig.3, and more quantitatively on Fig. 5, that the use of PNS resulted in higher yield stress than that obtained with PC, regardless of the type of cement. On the other hand, by comparing the yield stress values obtained after 8 and 60 min of age, it can be stated that the use of PC type resulted in maintaining a constant yield stress during 60 minutes after mixing with all types of cement. However, when the PNS is used a considerable increase in the yield stress is observed after 60 minutes of age. It must be mentioned, that the use of NO cement resulted in lower yield stress than in case of LH and BC, regardless of the type of superplasticizer (PC vs. PNS).

3.3 DISCUSSION

The pseudo-plastic behavior of solid particles suspension is generally explained by the order-disorder state and flocculated-deflocculated system. The order state results in a shear thinning flow characterized by a decrease of apparent viscosity with shear rate. In this case, the hydrodynamics forces, due to the shearing effect, are enough to overcome the attractive forces and ensuring a dispersed system [3]. The shear thickening is generally associated with highly concentrated suspension [4], where a disorder state is likely to be predominant, especially when increasing the shear rate regime. The shear thickening behavior of cement-based system may also be due to the presence of chemical admixtures. Indeed, under the shear effect, a linear-rigid polymer may be oriented in the flow direction by a rotation spin (disorder) while a flexible polymers is oriented in the flow direction by linear translation [5]. On the other hand, the adsorbed polymer may be desorbed when the shear rate increases, thus may increase the intrinsic viscosity of the solution.

3.4 EFFECT OF CEMENT-SUPERPLASTICIZER COMBINATION ON FILTRATION PROPERTIES (FORCED BLEEDING)

The use of low W/C structural cement grouts to ensure better structural performance is actually a common practice. For such a new class of grout, the standard test (JSCE-F-532-1994) used to evaluate the static bleeding resistance of fresh grout may be therefore irrelevant. On the other hand, cement grouts cast under pressure (pumping) or cast in vertical section can undergo some separation between cement particles and water, thus allow particles to sediment and water to bleed. The bleeding in such "dynamic" state is referred to the forced bleeding. The forced bleeding test used in this study consists in sustaining 300-mL sample of fresh grout under a pressure ranging between of 0.50 and 0.55 MPa for 10 minutes. As shown in Fig.6, the forced bleeding increases with the W/C, regardless of the cement-superplasticizer combination in use.

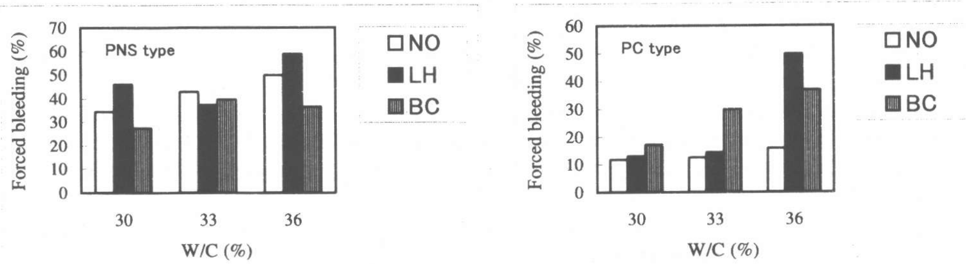

Fig. 6 Effect of W/C on the forced bleeding of grouts made with PNS and PC

Grouts made NO and LH cements exhibited good ability in resisting to the water removal compared to those made with BC cement, especially when the PC superplasticizer is used. However, when the PNS type is used all combinations showed a relatively high bleeding under pressure. This is may be due to the absorption bond of the polymers onto cement particles and their ability in ensuring a well-dispersed system. Indeed, the forced bleeding is related to the free water into the system and the distribution of particles in the system. A good dispersion may ensure better packing against the filter, thus reducing the permeability of the fresh grout and the bleeding.

4. CONCLUSIONS

Based on the results presented in this paper, the following conclusions can be warranted:

1. Compatibility/incompatibility phenomena as described in the literature are successfully reproduced for a wide range of W/C.
2. Regarding the achievement of high initial mini slump and good fluidity retention, PC type was more efficient than PNS, regardless of the type of cement. Such efficiency is traduced by a small change in the yield stress over 60 min of age.
3. The PC type is suitable for use with the three types of cement. However, in regards to the shear thickening behavior and the required dosage of superplasticizer to achieve a given fluidity, the LH-PC combination may be preferable.
4. The degree of shear thickening behavior is affected by the W/C as well as the cement-superplasticizer combination in use. The LH-PC combination showed the lowest degree of pseudoplasticity.
5. The grouts made with NO-PC and LH-PC combinations may be suitable in terms of the resistance to the forced bleeding for the range of W/C considered in this study.

REFERENCES

1. Yamada, K., Hanehara, S., and Honma, "The Effects of Naphthalene Sulfonate Type and Polycarboxylate Type Superplasticizers on the Fluidity of Belite-Riche Cement Concrete," Proceeding of the International Workshop on Self Compacting Concrete, August 1998, Kochi, Japan, 201-210.
2. Byungi-Gi, K., Shiping, J., Jolicoeur, C., and Aticin, P.C., "The Adsorbtion Behavior of PNS Superplasticizer and its Relation to Fluidity of Cement Paste," Cement and Concrete Research Journal, Vol. 30, No. 6, June 2000, pp. 887-893.
3. Robinson, J.V., "The Viscosity of Suspension of Spheres: Sediment Volume as a Determining Parameter," Transaction of the Society of Rheology, Vol. I, 1957, pp. 15-24.
4. Barnes, H.A., "Shear-Thickening "Dilatancy" in Suspension of non-Aggregation Solid Particles Dispersed in Newtonian Liquids," Journal of Rheology, Vol. 33, No. 2, 1989, pp. 329-366.
5. Courraze, G., and Grossiord, J.L., "Initiation to the Rheology," (available in French), Lavoisier TEC&DOC, 2nd Edition, Paris 1991.
6. De Kee, D., and Chan Man Fong, C.F., "Rhelogical Properties of Structured Fluids," *Polym. & Engineering Science*, 34 (1994) 438 p.