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Cement and Concrete Research 33 (2003) 1229–1234

CEMENT AND CONCRETE RESEARCH

Influence of time addition of superplasticizers on the rheological properties of fresh cement pastes

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Received 13 June 2002; accepted 22 January 2003

Abstract

It is well known that the fluidity and the fluidity loss of fresh cement pastes are affected by the kind and the time of addition of organic admixtures. The influence of the time addition of two chemical admixtures, namely, melamine formaldehyde sulfonate (MFS) and naphthalene formaldehyde sulfonate (NFS), on the rheological properties of ordinary Portland and sulfate-resisting cement pastes through the first 120 min of hydration was investigated. The admixture addition was delayed by 0, 5, 10, 15, 20, and 25 min. Shear stress and apparent viscosity of the cement pastes were determined at different shear rates (3–146 s^{-1}) and hydration times of 30, 60, 90, and 120 min. The concentration of Ca^{2+} and the combined water content of the cement pastes were determined after 120 min. Yield stress and plastic viscosity values were also determined by using the Bingham model. The results show that an increase in the addition time of the admixture reduces the shear stress, the yield stress, and the plastic viscosity of the cement pastes at the early ages (15 min) as well as at later early ages (120 min). The optimum delaying time of admixture addition is found to be 10–15 min. This time does not depend on the cement and superplasticizer type.

Keywords: Cement pastes; Rheology; Admixture; Yield stress; Plastic viscosity

1. Introduction

The high workability, using traditional superplasticizers based on melamine formaldehyde sulfonate (MFS) and naphthalene formaldehyde sulfonate (NFS), is lost in about 30 min, depending mainly on the admixture dosage, unless new polycarboxylate-based superplasticizers are used [1] and many other papers are made available in the literature. The loss of the workability occurs due to the formation of some hydrates in the early mixing and coagulation of lyophobic cement particles, thereby thickening the liquid phase and increasing the viscosity [2,3].

Some methods that can be adopted to prevent workability loss include the following:

- Delaying the addition of admixtures;
- Split dosing of the admixtures;
- Using cement with supplementary cementitious materials; and
- Using of other admixtures.

By delaying the addition of the admixtures to the concrete mix, the water molecules are quickly adsorbed by reactive cementitious particles, and the hydrated cover on these elements is formed beforehand: the C_3S and C_2S can adsorb sufficient SP molecules for their dispersion. The delaying time may be from 5 to 15 min [4]. The optimum time of the addition of naphthalene and melamine-based SP is considered to be at the beginning of the dormant period [5].

High-performance concrete (HPC) typically has a low water-to-cement (w/c) ratio and is produced in order to achieve the desired levels of strength and durability [6]. HPC has a tendency to be stiff and to lose its workability rather quickly. Often high-range water-reducing admixtures (HRWRAs) are used to improve the workability of HPC. HRWRA improves the workability and maintains strength; the results indicated that significantly higher slumps were found when the proportion of HRWRA was added after 20 min of mixing than when initially added.

Ramachandran et al. [7] discussed the factors affecting the efficiency of retarders with cement. They included the ratio of the retarder to cement, the time at which the retarder is added, and the temperature and composition of the cement. The time of initial set increases with the retarder

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doi:10.1016/S0008-8846(03)00037-1

content and generally decreases with temperature and cement content. Retarders are more effective with cements low in aluminate because the latter, or their hydration products, consume disproportionate amounts of retarder. Some are more effective with cements low in alkali perhaps because the latter destroys them. Retarders are most effective if added 2–4 min after mixing because the aluminate has, by that time, reacted to some extent with the gypsum and consumes a less amount of retarder.

It is well known that the fluidity and setting of fresh concrete are affected by the kind and time of addition of organic admixtures [8]. The fluidity, setting time, and time dependency of fluidity using fresh cement pastes with four kinds of organic admixtures by two different methods of addition (simultaneous and later addition) are estimated in order to clarify the influence of the kind and time of addition of admixture on the properties of fresh cement paste.

In the cement pastes containing a given dosage of NFS superplasticizer [8], it was found that the lower the amount of admixture adsorbed by cement, the larger the paste flow. It has also been shown by Kim et al. [9] that the slump and slump retention are related to the amount of "free" or available excess superplasticizer in the interstitial solution (phase) of fresh cement paste. Jolicoeur et al. [10] confirmed these results. There appears to be a direct relationship between the amount of PNS adsorbed and rate of the slump loss [1]. The amplitude of the effects of PNS depends on cement composition [11]. The retardation is confirmed to be strongly dependent on the C_3A content, in agreement with the finding of Hanna et al. [12] from fluidity data. It has also been found that the initial flow is mainly governed by the fineness and C_3A content of the cement [13].

In an earlier publication [14], the effect of delaying the addition of some concrete admixtures on the rheological properties of cement pastes during the initial 15 min of hydration has been studied, in which the admixture addition was delayed by 1, 3, 6, 10, and 13 min. The aim of the present investigation was to evaluate the relative effectiveness of delaying addition on the rheological and adsorption properties of cement pastes during the initial 120 min of hydration. The addition of admixtures was delayed by 5, 10, 15, 20, and 25 min.

2. Experimental

2.1. Materials

2.1.1. Cements

Ordinary Portland cement (OPC) and sulfate-resisting cement (SRC) were supplied by Helwan Portland Cement. Table 1 presents the chemical composition of OPC and SRC. The Blain surface area was 3054 and 3067 cm^2/g for OPC and SRC, respectively.

The phase composition, calculated from Bogue's equations, was: $C_3S = 50\%$, $C_2S = 23\%$, $C_3A = 8.6\%$, and $C_4AF = 10.4\%$ for OPC; and $C_3S = 67.5\%$, $C_2S = 9.8\%$, $C_3A = 1.45\%$, and $C_4AF = 15\%$ for SRC.

Table 1
Chemical oxide composition of the starting materials (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
OPC	21.05	5.45	3.42	63.41	2.09	2.39	0.18	0.09	1.90
SRC	20.88	3.70	4.94	64.57	2.00	1.62	0.02	0.04	2.27

2.1.2. Commercial superplasticizers

(a) Melment L10 is a commercial superplasticizer. Its chemical composition is MFS, supplied by Modern Building Materials as a white solid material and used as 12.5% solution.
(b) NFS is a commercial superplasticizers. Its chemical composition is sodium salt of NFS, supplied by Modern Building Materials as a brown solid material and used as 12.5% solution.

2.2. Rheological measurements

The cement pastes were prepared by mixing exactly 50 g of cement in a porcelain dish together with a constant amount of the MFS or NFS admixtures (1.0 wt.% cement). The w/c ratio was 0.30. Only 75% of the mixing water was initially added and the rest of mixing water containing the admixtures were added after delaying times of 0, 5, 10, 15, 20, and 25 min. The measurement was done during 120 min of hydration. Shear stress values, as well as apparent viscosity of different cement pastes at different shear rates and hydration times, were obtained using Rheotest 2.1 Apparatuse (Germany).

2.3. Ca^{2+} concentration and chemically combined water

In this program OPC, MFS and distilled water were used and the w/c ratio was 5.0. Only 95% of the mixing water was initially added and the addition of the remainder containing the MFS was delayed by 0, 5, 10, 15, 20, and 25 min. The slurries were mechanically stirred for 120 min using a mechanical stirrer at a speed of 300 rpm, and the sample solution was separated by suction filter. The chemically combined water content was determined after stopping the hydration of the paste [15] and the Ca^{2+} concentrations were immediately determined by ICP at $\lambda = 373.69$ nm.

3. Results and discussion

3.1. Rheological measurement

The rheological behavior of a fluid such as cement paste, mortar, or concrete is most often characterized by at least

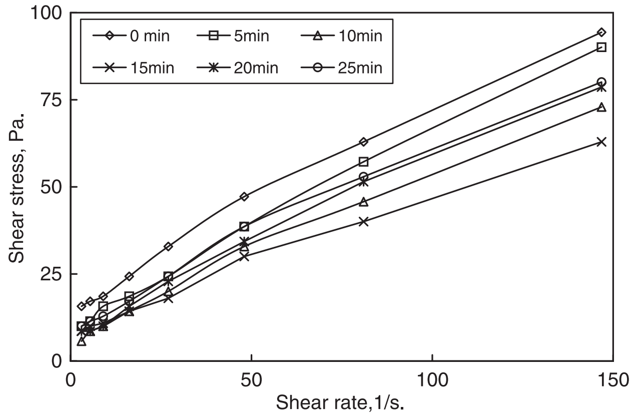

Fig. 1. Shear stress–shear rate relationship of OPC pastes admixed with 1% MFS at different delaying times (hydration of 30 min).

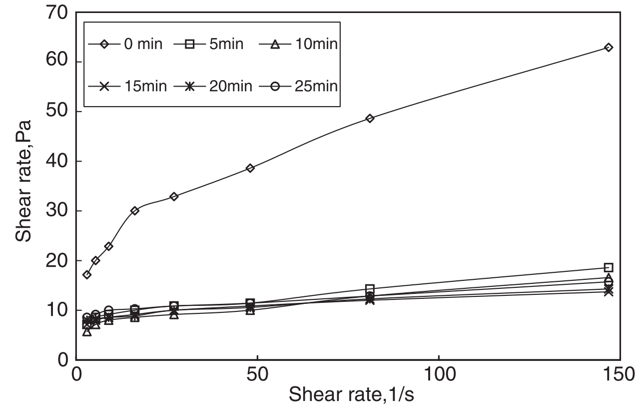

Fig. 3. Shear stress–shear rate relationship of SRC pastes admixed with 1% MFS at different delaying times (hydration time of 30 min).

two parameters, τ_0 and μ, as defined by the Bingham equation [16]:

$$\tau = \tau_0 + \mu\gamma$$

In this equation, τ is the shear stress (Pa), τ_0 is the yield stress (Pa), μ is the plastic viscosity (Pa s), and γ is the shear rate (s^{-1}). The yield stress and the plastic viscosity are the Bingham parameters that characterize the flow properties of the materials.

The rheological data of the OPC and SRC pastes admixed with 1.0 wt.% MFS and NFS admixtures, added by simultaneous as well as later addition at an interval time of 30 min, are represented in Figs. 1–5.

Figs. 1 and 2 show the shear stress and apparent viscosity of OPC pastes admixed with 1.0 wt.% MFS added at delaying times of 0, 5, 10, 15, 20, and 25 min. It is clear that the shear stress values increase with shear rate and decrease with delaying time up to 15 min. The maximum shear stress values (at a maximum shear rate of 146.8 s^{-1}) were 94, 90, 73, 63, 79, and 80 Pa for delaying times of 0, 5, 10, 15, 20, and 25 min, respectively. The reduction in shear stress values was 4.5, 23, 33, 17, and 15 for delaying times of 5, 10, 15, 20, and 25 min, respectively.

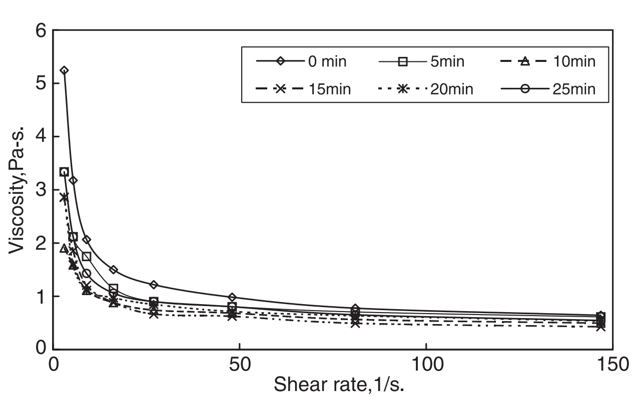

Fig. 2. Viscosity–shear rate relationship of OPC pastes admixed with 1% MFS at different delaying times (hydration time of 30 min).

Fig. 2 illustrates the apparent viscosity of OPC pastes admixed with 1.0 wt.% MFS. The apparent viscosity of all OPC pastes decreases with the shear rate up to 16 s^{-1} and then nearly has constant values; this is clear in the pastes prepared by simultaneous addition of admixture with mixing water. On the other hand, the change in apparent viscosity is very small for the pastes prepared at delayed additions. Also, the apparent viscosity of cement pastes decreases with delaying time up to 15 min. The minimum apparent viscosity values of cement pastes (at a shear rate of 146.4 of s^{-1}) were 0.61, 0.49, 0.42, 0.53, and 0.54 Pa s for delaying times of 0, 5, 10, 15, 20, and 25 min, respectively.

The shear stress of SRC pastes admixed with 1.0 wt.% MFS with delaying times is seen in Fig. 3. It is clear that the shear stress of SRC pastes decreases with delaying addition of the admixture. Also, as the delaying time increases, the obtained shear stress decreases up to 15 min. The maximum shear stress values were 63, 18.6, 16.6, 15.7, 15.4, and 15.7 Pa for delaying times of 0, 5, 10, 15, 20, and 25 min, respectively. The reduction in the shear stress values were 70%, 74%, 75%, 75%, and 75% for delaying times of 5, 10, 15, 20, and 25 min, respectively.

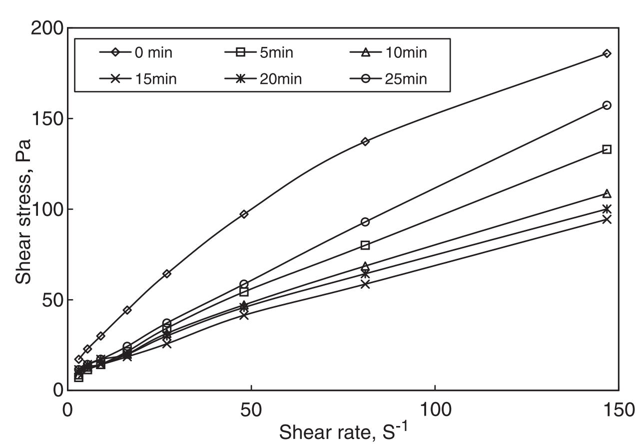

Fig. 4. Shear stress–shear rate relationship of OPC pastes admixed with 1% MFS at different delaying times (hydration time of 120 min).

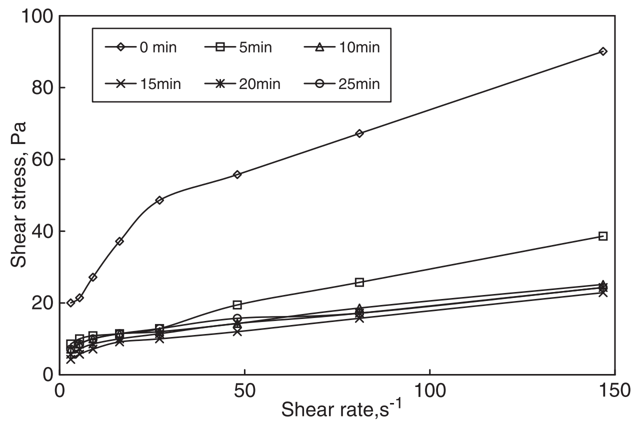

Fig. 5. Shear stress–shear rate relationship of SRC pastes admixed with 1% MFS at different delaying times (hydration time of 120 min).

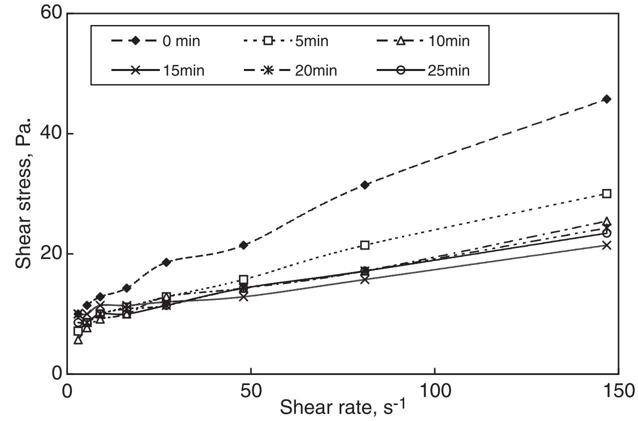

Fig. 6. Shear stress–shear rate relationship of OPC pastes admixed with 1% NFS at different delaying times (hydration time of 30 min).

Figs. 4 and 5 illustrate the shear stress–shear rate relationships of OPC and SRC pastes admixed with 1% MFS after a hydration time of 120 min. As shown in Fig. 4, the obtained shear stress decreases by increasing the delaying addition time up to 15 min. The maximum shear stress values were 186, 133, 109, 94, 100, and 157 Pa for delaying addition times of 0, 5, 10, 15, 20, and 25, respectively. Also it is clear that 15 min is the optimum delaying addition time.

Fig. 5 shows the obtained shear stress of SRC pastes admixed with 1% MFS after a hydration time of 120 min. The maximum shear stress values were, 90, 39, 25, 23, 24, and 24 Pa for admixture addition delaying times of 0, 5, 10, 15, 20, and 25 min, respectively. Its clear that the delaying time of 15 min has the lowest shear stress values.

As shown in Figs. 4 and 5, it is clear that the optimum delaying addition time of MFS is 15 min for OPC and SRC pastes. Also delaying the admixture addition enhances the fluidity of the OPC pastes, after 30 and 120 min of hydration. The effect of the MFS on SRC pastes is more than OPC pastes. This may be due to the lower C_3A content in SRC than OPC.

As shown in Table 2, the shear stress values increase with hydration time (30 and 120 min) for both simultaneous and delayed addition (I and II). The maximum shear stress values were 94 and 186 Pa for simultaneous addition for hydration times of 30 and 120 min, and 63 and 94 Pa for a delaying time of 15 min and for hydration times of 30 and 120 min, respectively. The increases in shear stress values were 98% and 49% for delaying addition times of 0.0 and 15 min; this means that delaying the admixture addition reduces the fluidity loss of the OPC pastes to half the value of its simultaneous addition, during the initial 2 h of hydration.

The effect of delayed addition of NFS on the shear stress values of OPC pastes was graphically plotted in Fig. 6. It shows the obtained shear stress values of OPC pastes prepared with and without later addition of NFS. Its is clear also that the shear stress values are reduced by increasing the delaying addition time up to 15 min. The maximum shear stresses were 46, 30, 25, 21, 24, and 23 Pa for delaying times of 0, 5, 10, 15, 20, and 25 min, respectively.

The results of the OPC pastes admixed with 1.0 wt.% MFS or NFS show nearly the same behaviour. It can be concluded that the delayed addition of 1.0 wt.% MFS or NFS after 15 min gives better rheological properties of the cement pastes.

Table 3 shows the yield stress (τ_0) and plastic viscosity (μ) of the different cement pastes from the Bingham model in low shear rates (0–50 s^{-1}). It is clear that the yield stress as well as the plastic viscosity values decrease by delaying the admixture addition. In general, as the delaying time of admixture addition increases, the τ_0 and μ decrease (fluidity increases) up to 10–15 min.

Table 2
Shear stress for OPC pastes admixed with 1% MFS at hydration times of 30 and 120 min for delaying times of 0 min (I) and 15 min (II)

Shear rate (s^{-1})	Shear stress (Pa)			
	I—30	I—120	II—30	II—120
3.0	16	17	9	10
5.4	17	23	10	13
9.0	19	30	11	14
16.2	24	44	14	19
27.0	33	64	18	26
48.0	47	97	30	41
81.0	63	137	40	59
146.8	94	186	63	94

Table 3
The yield stress and plastic viscosity of different cement pastes at different delaying times after a hydration time of 30 min

Delaying time (min)	OPC/MFS		SRC/MFS		OPC/NFS	
	τ_0	μ	τ_0	μ	τ_0	μ
0	13.1	0.71	14.47	0.96	10.2	0.253
5	8.6	0.62	7.1	0.19	7.72	0.176
10	4.7	0.59	5.7	0.2	6.77	0.176
15	6.9	0.47	7	0.14	9.66	0.075
20	5.8	0.6	7.9	0.06	7.83	0.14
25	7.5	0.64	8.49	0.13	7.82	0.14

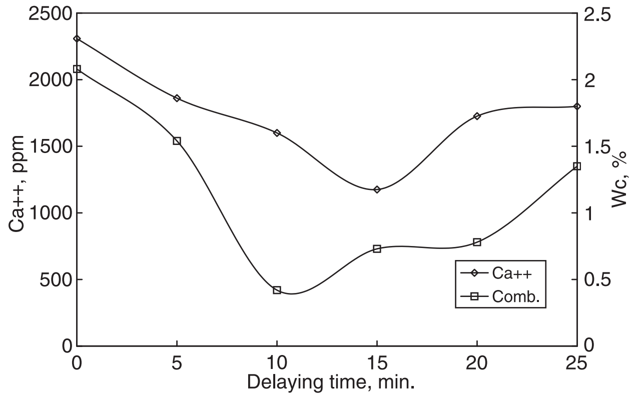

Fig. 7. The combined water and Ca^{2+} concentration of OPC pastes admixed with MFS at different delaying times.

The delaying admixture addition, enhancing the fluidity of cement pastes, may be due to the following: (i) C_3A, which is responsible for lowering the fluidity by its rapid (instantaneous) hydration at early age (i.e., C_3A content is minimized by hydration for 10 min); and (ii) the admixture adsorption on unhydrated C_3S and C_3A is higher than that on hydrated phases [8]. In other words, the positive sites of aluminate phases C_3A or/and C_4AF, which are responsible for consuming the MFS or NFS, are reduced on progressive hydration. Delayed addition of superplasticizers acts as an additional repulsive barrier between the cement particles, with a further contribution to improve the fluidity of the cement pastes.

3.2. Ca^{2+} ion concentration and chemically combined water

It is well known that as the hydration time proceeds, the liberated free lime increases. For constant hydration time (120 min), it is clear from Fig. 7 that the Ca^{2+} ion concentration of sample solution decreases with delayed admixture addition time up to 15 min. This means that the hydration rate of cement pastes decreases with delaying time. This is confirmed by determining the chemically combined water of dried cement pastes, which also decreases by increasing the delaying time as shown in Fig. 7.

The higher the amount of admixture adsorption on cement paste, the higher the amount needed for constant fluidity [8]. Therefore, the pastes of 10–15 min delaying time possess the lower amount of admixture adsorbed at constant fluidity. These results are in a good agreement with the rheological values and those of previous work [14]. The chemically combined water content decreases with delaying time up to 10 min; this is due to retardation of paste hydration. As shown in Fig. 7, at a constant time of hydration and a high w/c ratio, the freer is the admixture in the interstitial phase, the more that the retardation of cement paste hydration occurs. This is due to the fact that delaying the admixture addition enhances the adsorption of dissolved sulfate ion on the positive sites of C_3A and C_4AF. This leads to a decrease of the adsorption of NFS and MFS.

4. Conclusions

The following conclusions can be drawn from the current work:

1. Delaying the admixture addition increases the rheological properties of the cement pastes not only for a short time (30 min) but also for a long time (120 min).
2. The decrease of the yield stress and plastic viscosity of cement pastes depends on the examined cement composition and delaying time of admixtures.
3. The optimum delaying admixture addition time is 10–15 min (after the initial mixing of the water) for examined Portland cements and admixtures.

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