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Effect of delaying addition of some concrete admixtures on the rheological properties of cement pastes

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Abstract

The effect of delayed addition of two concrete admixtures, namely melamine formaldehyde sulfonate (MFS) and naphthalene formaldehyde sulfonate (NFS), on the rheological and adsorption properties of ordinary Portland cement (OPC), sulfate-resisting cement (SRC) and silica fume-ordinary Portland cement (SF-OPC) pastes was investigated. The admixture addition was delayed by 1, 3, 6, 10 and 13 min after the addition of mixing water. The shear stress, as well as the apparent viscosity of these cement pastes, was determined at different shear rates. Total organic carbon (TOC), Ca^{2+} concentration and conductivity of the filtrate and the combined water content of the precipitated cement pastes were determined. The results show that delaying the admixtures addition increases the cement pastes workability than that of simultaneous addition.

Keywords: Rheology; Concrete admixture; Delaying addition; Shear stress; Shear rate; Apparent viscosity

1. Introduction

High-performance concretes (HPCs) typically have low water/cement ratio (w/c) in order to achieve the desired levels of strength and durability [1]. As a result, HPCs have a tendency to be stiff and to lose their workability rather quickly. Often, high-range water-reducing admixtures (HRWRA) are used to improve the workability of OPC. It was found that although retempering concrete with HRWRA would generally improve the workability and maintain the strength of low w/c concretes. The results indicated that significantly higher slumps were found when the proportion of HRWRA added after 20 min of mixing than that initially added.

The effect of a two-step mixing method upon the properties of concrete mixtures containing superplasticizing admixtures has been investigated [2]. The properties of the two-step mixed concrete and conventional concrete are compared. At 28 days of age, concrete mixed by the two-step mixing method showed about 8–17% higher compressive strength than the one mixed by the normal method. Two-step mixing methods are used to improve the properties of concrete. This benefit is presumably attributable to more efficient hydration of the cement resulting from the more intimate contact between cement particles and water achieved in the vigorous blending of cement paste. The later addition of concrete admixtures is regarded as a useful measure to improve workability and decrease the water–cement ratio of concrete, and thereby relative high strength.

It is well known that the fluidity and setting of fresh concrete are affected by kind and added timing of organic admixtures including fluidizing agents and water-reducing agents [3]. The fluidity, setting time and time dependency of fluidity using fresh cement paste were prepared with four kinds of admixtures by two different methods of addition (simultaneous and later addition). Hydration, adsorptive behaviour of admixture to the clinker minerals and the structure of cement paste are also estimated in order to clarify the influence of kind and added times of admixture on the properties of fresh cement paste.

In the cement pastes containing a given dosage of naphthalene formaldehyde sulfonate (NFS) superplasticizer [4], it was found that the lower the amount of admixture

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

Cements	Oxide								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	I. L.*
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
SF	94.64	0.97	0.93	0.55	0.35	0.10	0.20	0.25	2.02

* Ignition Loss

adsorption by cement paste, the larger the paste flows. It has been also shown by Jolicoeur et al. [5] 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. These results were confirmed by Yamada et al. [6]. It appears to be an inverse relationship between the amount of PNS adsorbed and rate of the slump loss (which is related to rheology) [4].

The amplitude of the effects of PNS depends on cement composition [7]. The retardation is confirmed to be strongly dependent on C_3A content, in agreement with the finding of Hanna et al. [8] from fluidity data. In addition, the fineness and C_3A content of the cement [9] mainly govern the initial flow.

The aim of the present investigation was to evaluate the relative effectiveness of delayed addition of two concrete admixtures on the rheological and adsorption properties of ordinary Portland cement (OPC), sulfate-resisting cement (SRC) and silica fume-ordinary Portland cement (SF-OPC) pastes.

2. Experimental

OPC and SRC, supplied by Helwan Portland Cement, as well as silica fume (SF) supplied by Ferro-Silicon Alloy, Edfo, Kom Ombo, Egypt, were used in this investigation. Blended cement was prepared by replacing 10% OPC by SF.

Table 1 shows the chemical composition of the OPC, SRC and SF. The surface area was 3054 and 3067 cm^2/g for OPC and SRC, respectively, and 20 m^2/g for SF.

The phase composition was calculated from Bogues equation as follows:

	OPC (%)	SRC (%)
C_3S	50	67.5
C_2S	23	9.8
C_3A	8.6	1.45
C_4AF	10.4	15

2.1. Rheological measurements

The cement pastes were prepared by mixing exactly 50 g cement in a porcelain dish, together with constant solid dry amount of the melamine formaldehyde sulfonate (MFS) and NFS admixtures (1.0 cement mass%). The w/c was 0.30 for OPC and SRC pastes and 0.40 for SF-OPC pastes; 75% of the mixing water was initially added, and the rest containing the admixtures was added after delaying times of 1, 3, 6, 10 and 13 min. Measuring was done after 15 min of mixing. Shear stress values, as well as apparent viscosity of different cement pastes at different shear rates, were obtained using Rheotest 2.1.

2.2. Adsorption measurements

In this program, OPC, MFS and distilled water were used. The w/c was 5.0; 95% of this amount of mixing water was initially added, and the rest containing the MFS was added after delaying times of 1, 3, 6, 10 and 13 min. The slurries were mechanically stirred for 30 min using a mechanical stirrer at speed of 300 rpm, and the sample solution was separated by a suction filter. The chemically combined water content was determined after stopping the hydration of the paste [10]. The conductivity of the solutions were determined using immersion electrode conductimeter of type Crison-8401, the Ca^{2+} concentrations were determined by ICP at $\lambda = 373.69$ nm. The total organic carbon (TOC) remaining in the solutions was also determined using TOC 1200 analyzer.

3. Results and discussion

3.1. Rheological properties

The rheological data of the OPC, SRC and SF-OPC blended pastes admixed with 1.0 wt.% of cement of two organic admixtures, namely MFS and NFS added by simultaneous as well as later addition are represented in Figs. 1–4. Figs. 1 and 2 show the shear stress and apparent viscosity of OPC pastes admixed with 1.0 wt.% MFS added at delaying times 0, 1, 3, 6, 10 and 13 min. It is clear that the

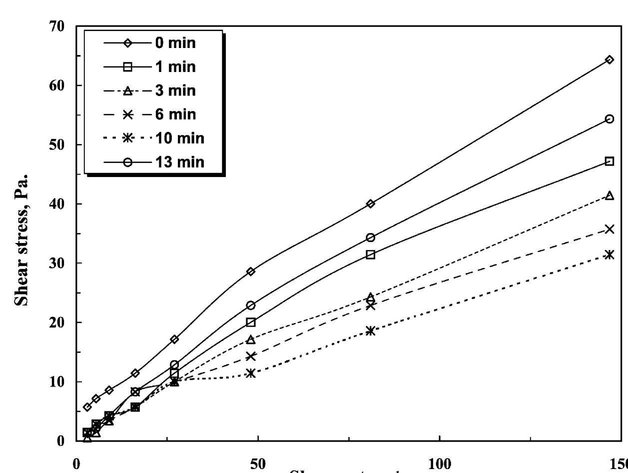

Fig. 1. Shear stress–shear rate relationship of OPC pastes admixed with 1% MFS at different delaying times.

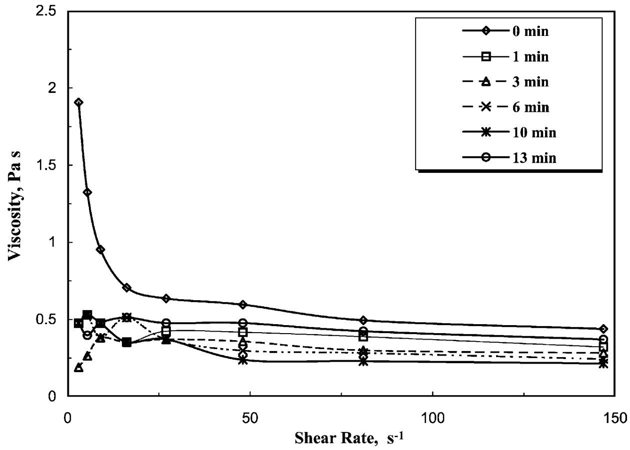

Fig. 2. Viscosity–shear rate relationship of OPC pastes admixed with 1% MFS at different delaying times.

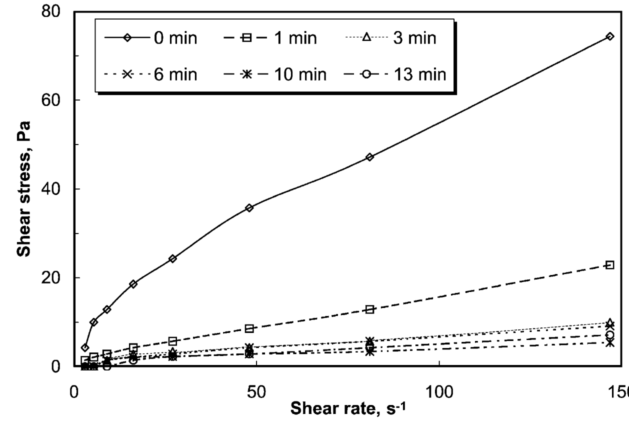

Fig. 4. Shear stress–shear rate relationship of SF-OPC pastes admixed with 1% MFS at different delaying times.

shear stress values increase with shear rate and decrease with delaying time up to 10 min. The maximum shear stress values (at maximum shear rate 146.8 s^{-1}) were 64, 47, 42, 36, 32 and 54 Pa for delaying times of 0, 1, 3, 6, 10 and 13 min, respectively. The reduction in shear stress values was 27, 34, 44, 51 and 15 for delaying times of 1, 3, 6, 10 and 13 min, respectively.

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 constant values were obtained. 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 addition. In addition, the apparent viscosity of cement pastes decreases with a delaying time up to 10 min. The maximum apparent viscosity values of cement pastes (at shear rate of 146.4 s^{-1}) were 0.44, 0.32, 0.28, 0.24, 0.21 and 0.37 Pa s for delaying times of 0, 1, 3, 6, 10 and 13 min, respectively.

The shear stress value of SRC pastes admixed with 1.0 wt.% MFS with delayed times are seen in Fig. 3. It is clear that the shear stress value of SRC pastes decreases with delaying addition of the admixture. In addition, as the delaying time increases, the obtained shear stress decreases up to 10 min and then increases at 13 min. The maximum shear stress values were 60, 31, 20, 15, 9 and 14 Pa for delaying times of 0, 1, 3, 6, 10 and 13 min, respectively. On the other side, the reduction in the shear stress values were 47.6%, 66.7%, 73.8%, 85.7% and 76.2% for delaying times 1, 3, 6, 10 and 13 min, respectively.

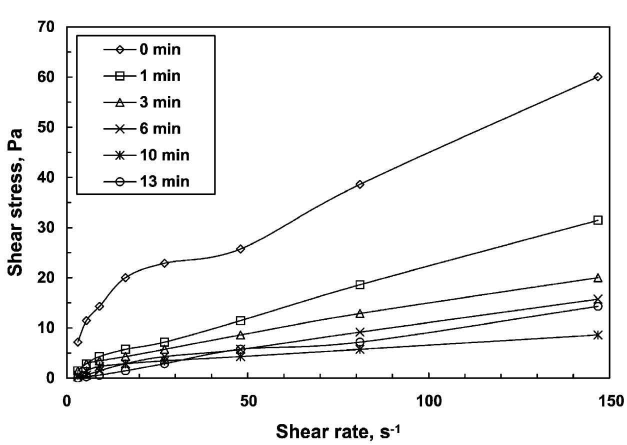

Fig. 3. Shear stress–shear rate relationship of SRC pastes admixed with 1% MFS at different delaying times.

Fig. 4 illustrates the shear stress values of SF-OPC pastes admixed with 1.0 wt.% MFS by simultaneous and delayed addition. As shown in Fig. 4, it is clear that the obtained shear stress of cement pastes decreases sharply with delaying times up to 10 min. The maximum shear stress values were 74, 23, 10, 9, 5 and 7 Pa for delaying time of 0, 1, 3, 6, 10 and 13 min, respectively.

The results of Figs. 1, 3 and 4 illustrate that the shear stresses values of OPC are higher than those of SRC and SF-OPC pastes. The reduction in shear stresses by delayed addition of 1.0 wt.% of MFS to OPC, SRC as well as SF-OPC pastes were 27%, 34%, 44%, 50% and 15%; 48%, 67%, 74%, 85% and 76% and 69%, 87%, 88%, 93% and 90% for 1, 3, 6, 10 and 13 min, respectively. It is shown that SF-OPC pastes give the highest reduction and OPC pastes show the lowest values as shown in Fig. 5. The reduction in shear stress ranges between 41% and 75%, 83% and 92% and 88% and 100% for OPC, SRC and SF-OPC pastes, respectively. Therefore, the later addition improves the workability of cement pastes admixed with 1.0 wt.% MFS in the order SF-OPC>SRC>OPC.

This may be due to the following: (1) C_3A%, which is responsible for lowering the fluidity by its rapid (instantaneous) hydration at early age. Therefore, C_3A is minimized by hydration before admixture addition till 10 min. (2) The admixture adsorption of unhydrated C_3S and C_3A is higher than that of hydrated phases [3], this increases the admixture ratio in the interstitial phase leading to an increase in cement paste workability.

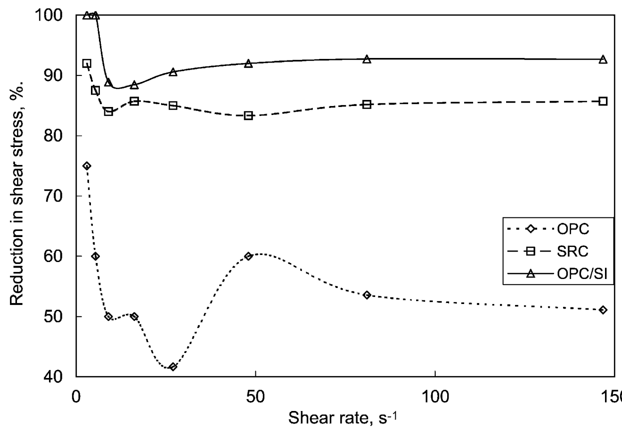

Fig. 5. Reduction in shear stress of different cement pastes admixed with 1% MFS at 10 min of delaying time.

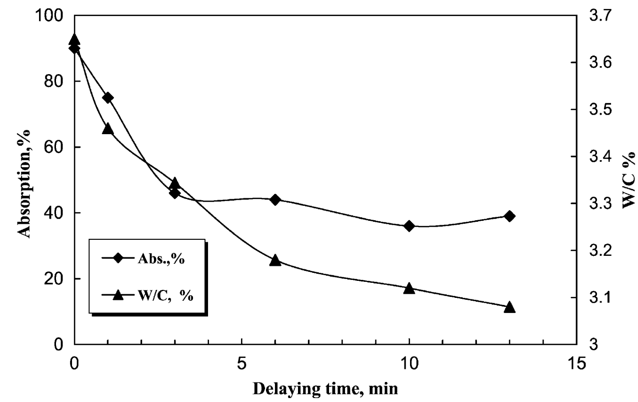

Fig. 7. The absorption and chemically combined water of OPC pastes admixed with 1% MFS at different delaying times.

By delaying the addition of the admixtures to the mix, the water molecules are quickly adsorbed in advance by reactive cementitious particles, and the hydrated cover on these elements is formed beforehand: The C_3S and C_2S can adsorb sufficient SP-HRWRA molecules for their dispersion. The delaying time may be from 5 to 15 min [11].

It was found in an earlier work that the addition of 0.75 wt.% MFS to SRC and SRC + SF decreases the water demand of the cement pastes [12]. The reduction of water demand was 20% and 50% for SRC and SRC + SF pastes, respectively. Therefore, admixture is more effective on SF-blended cement than SRC.

The effect of delayed addition of NFS on the shear stress values of OPC pastes was graphically plotted in Fig. 6. It is clear that the shear stress values reduce with the delayed addition and decrease with the time up to 10 min then remain constant at 13 min. The maximum shear stresses values were 70, 53, 40, 40, 36 and 36 Pa for delaying times of 0, 1, 3, 6, 10 and 13 min, respectively. The reduction in the shear stress values was 24%, 43%, 43%, 49% and 49% for delaying times 1, 3, 6, 10 and 13 min, respectively.

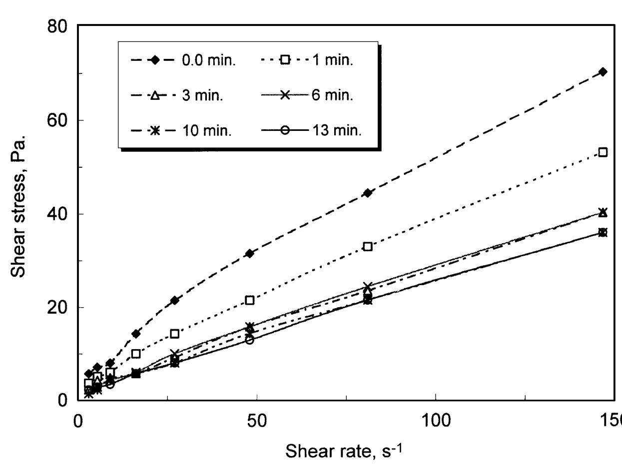

Fig. 6. Shear stress–shear rate relationship of OPC pastes admixed with 1% NFS at different delaying times.

3.2. Adsorption properties

3.2.1. Total organic carbon

The adsorption of MFS on the OPC pastes was determined from TOC in the sample solutions. Fig. 7 shows the adsorption percent of MFS on OPC pastes. It is clear that the delayed addition of the admixture reduces the adsorption percent up to 10 min. The adsorption percentages were 90%, 75%, 46%, 44%, 36% and 39% for delaying times of 0, 1, 3, 6, 10 and 13 min, respectively. The results of the adsorption percent of MFS are in good agreement with those of shear stress and apparent viscosity values, i.e. 10 min shows the maximum time of delayed mixing of the MFS.

The higher the amount of admixture adsorption by cement paste the higher amount needed for constant fluidity [3]. Therefore, the paste of the 10-min delaying time has the lower amount of admixture adsorbed at constant fluidity. These results are in good agreement with the rheological values. In addition, the chemically combined water decreases with delaying time up to 10 min; this is due to the retardation of pastes hydration, as shown in Fig. 7. At constant time of hydration and w/c, the freer admixture in

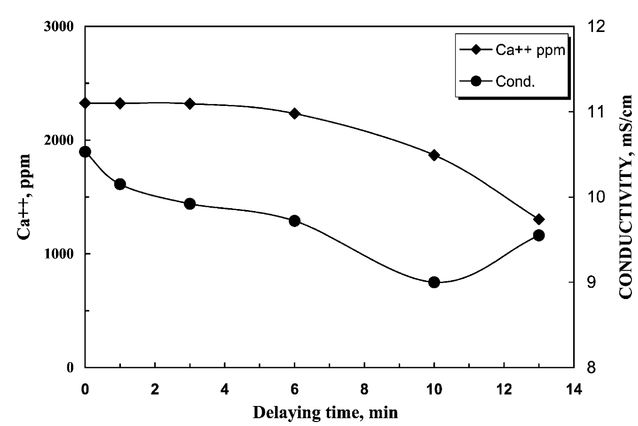

Fig. 8. The Ca^{2+} concentration and electrical conductivity of OPC pastes admixed with 1% MFS at different delaying times.

the interstitial phase, the more retardation of cement paste occurred. 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 decreases the adsorption properties of PNS and MFS.

3.2.2. Ca^{2+} concentrations and electrical conductivity

The electrical conductivity of the solutions is due to the liberation of free lime during the paste hydration. Therefore, as the hydration time proceeds, the liberated free lime increases. Fig. 8 shows that at constant hydration time, the conductance of the sample solution decreases with delaying time up to 10 min. This means that the Ca^{2+} decreases with delaying time. This is confirmed by determined Ca^{2+} in the sample solution by ICP as shown in Fig. 8.

4. Conclusions

1. Delaying the admixture addition enhances the rheological and adsorption properties of the cement pastes.
2. The enhancement in the rheological properties of cement pastes depends on the cement composition and delaying time.
3. The optimum delaying admixtures addition time is 10 min after mixing the water for all cements and admixtures.
4. The mechanism of enhancing the rheological and adsorption properties of cement pastes needs a lot of work to clarify it.

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