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Effect of addition time of a superplasticizer on cement adsorption and on concrete workability

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Abstract

The effect of addition time of a naphthalene-based superplasticizer (SNF) on the adsorption behavior on type I Portland cement slurries and on the concrete workability was studied. Test results indicate that the adsorption behavior of SNF on cement particles follows a Langmuir isothermal adsorption model. As the addition time increases, the saturated adsorption amount of SNF decreases sharply at the beginning and then more slowly. In comparison, the concrete workability decreases slightly in the early phase and then falls off abruptly. Most importantly, the transition points in both cases appear to be the same, at about 10–15 min. This strongly suggests that a close relationship exists between the SNF adsorption behavior on cement particles and the workability of concrete. In addition, the optimum addition time of SNF to concrete should be in this period, which corresponds to the beginning of the dormant period of the cement hydration process. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Superplasticizer; Cement; Adsorption; Addition time; Concrete; Workability

1. Introduction

High performance concrete (HPC) is a novel construction material which has recently been developed. As it enhances the properties of traditional concrete in terms of workability, mechanical strength and durability, HPC has been increasingly used in projects such as tall buildings, bridges and off-shore structures [1]. One key to the successful preparation of this new material is the addition of high-range water-reducing admixtures, known as superplasticizers, to the concrete. Sulfonated melamine formaldehyde condensates (SMF) and sulfonated naphthalene formaldehyde condensates (SNF) are two well-established commercial superplasticizers. These admixtures are claimed to exhibit good dispersing effects on concrete, and to be able to reduce water demand of concrete by up to 30%, while still maintaining the flow characteristics. Currently, a new generation of superplasticizers based on polycarboxylate polymers with long, comb-type side chains is claimed to allow for even more reduction of water content, up to 40%. This has led to the development of very low water/cement (W/C) ratio HPC [2,3].

The effect of superplasticizers on the workability of concrete has been ascribed to the ability of admixture molecules to be adsorbed on cement particles, thus providing a dispersing effect on the concrete. Factors such as the type and dosage of the superplasticizers, the nature and amount of cement and aggregates, the temperature and mixing procedure, as well as the addition time of the admixtures cause different fluidizing effects for the resulting cementitious materials [4]. Regarding the factor of addition time, Hewlett [5] reported that addition of superplasticizer resulted in decreased slump values for the period from 5 to 50 min after the concrete was in contact with water. In contrast, the results of Kasami et al. [6] showed that almost constant slump values were maintained for the delayed addition of their superplasticizers up to 60 min. They reasoned that the discrepancy might be due either to the difference in concrete mixtures or the difference in the performance of the superplasticizers. In addition, it was stated [7,8] that a slightly delayed addition would produce a more workable concrete or cement paste than an immediate addition. Uchikawa et al. [8] confirm that SNF polymer is adsorbed more, particularly on the C_3A hydration products, when the immediate addition procedure is

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adopted. The superplasticizing effect is improved with a delayed SNF addition because of the lower adsorption of the polymer on the C_3A hydration products. Meanwhile, Collepardi [9] finds that a preliminary treatment of cement with even a small amount of water produces superplasticized concrete mixes which perform as well as the best concrete produced by delayed addition. He explains that this effect would be related to the production of an ettringite coating on the surface of cement particles during the preliminary water treatment. Consequently, the adsorption of either SMF or SNF polymer molecules on the prehydrated cement surface is reduced and more superplasticizer molecules are left for dispersion of C_3S and C_2S. That causes the subsequent dispersion action to be more effective than that recorded in the absence of the preliminary water treatment [10]. Finally, the technique of redosing the superplasticizer at different intervals of time has also been developed. However, this method is mainly for reducing slump loss in field applications, and it appears to be not easily adopted or controlled in practice [9].

It is clear that the effectiveness of superplasticizers on concrete is strongly related to the adsorption behavior of the admixtures on cement particles, as well as the degree of hydration [11–14]. Furthermore, the mechanism of the action of superplasticizers added to aged concrete, although been studied, is not thoroughly understood. This leads to some limits on the use of these admixtures in practical applications. The present study was carried out to determine the proper time for addition of SNF superplasticizer based on its adsorption behavior for type I Portland cement slurries and on the workability tests of cement pastes and concrete.

2. Adsorption mechanism

A superplasticizer such as SNF is an anionic polymeric surfactant. When it is adsorbed on the surface of cement particles, only a monolayer of admixture molecules is possible because the negative charge-containing molecules would repel each other. Therefore the adsorption of SNF can be expected to follow Langmuir isotherms [7,11].

A Langmuir isotherm [15] assumes that: (1) the surface contains a set of sites on which only a single layer of adsorbed molecules is formed; (2) the total number of surface sites is fixed for a fixed amount of adsorbing particles, and (3) both the adsorption and desorption are elementary processes.

The adsorption process of SNF molecules on the surface sites of cement particles is represented by

$$\mathrm{SNF} + \text{surface site} \rightleftharpoons \mathrm{SNF(adsorbed)} \tag{1}$$

The rate of adsorption is $k_1[\mathrm{SNF}](1-\theta)$, and the rate of desorption is $k_2\theta$. At equilibrium, the rate of adsorption is equal to the rate of desorption, and the following equation can be derived.

$$1/\theta = B/M = 1 + 1/K[\mathrm{SNF}]\mathrm{eq} \tag{2}$$

or

$$1/M = 1/B + 1/BK[\mathrm{SNF}]\mathrm{eq} \tag{3}$$

where θ is the fraction of the surface sites occupied by adsorbed SNF molecules; k_1, k_2 and K are adsorption constant, desorption constant and equilibrium constant, respectively. M, B and [SNF]eq are the adsorbed amount, the saturated adsorbed amount and the concentration of SNF in slurry at equilibrium.

3. Experimental

3.1. Materials

Type I Portland cement, river sand and river stone (from midwest Taiwan) were used. Properties of cement and aggregates are given in Tables 1 and 2. A commercial SNF superplasticizer with 42.7% solid content was used as the chemical admixture.

3.2. Adsorption measurement from cement slurry

In doing the adsorption experiment, a dilute concentration of cement slurry is preferred because cement particles in the system would be fully separated without affecting each other in adsorbing admixture molecules. However, a very dilute cement concentration should be avoided. The hydration for cement concentration $\leqslant 1$ g/l is reported to differ significantly from the hydration under practical conditions [16]. Therefore, cement slurry in this study was prepared by mixing 1 g cement with 500 g water. Then 100 ml SNF aqueous solution was

Table 1
Properties of cement

Component	wt%
SiO_2	20.49
Al_2O_3	6.57
Fe_2O_3	3.27
CaO	62.40
MgO	1.91
SO_3	2.20
f-CaO	1.03
C_3S	43.2
C_2S	26.1
C_3A	11.9
C_4AF	9.95
Ignition loss	1.57
Blaine surface area	3013 (cm^2/g)
Specific gravity	3.14 (g/cm^3)

Table 2
Properties of aggregates

Property	Coarse aggregate	Fine aggregate
Specific gravity (g/cm^3)	2.63	2.63
Unit weight (kg/m^3)	1573	–
Fineness modulus	6.47	3.07
Absorption capacity (%)	0.95	2.13
Maximum size (mm)	19.1	5.6

added to the slurry at specific times at room temperature, the slurry was mixed again, and samples were taken periodically afterwards. The initial SNF concentration in the cement slurry under study ranged from 50 to 300 ppm. The amount of SNF adsorbed was determined by the difference in concentration of admixture in the liquid phase before and after adsorption. The SNF concentration was measured using a UV-spectrophotometer (Hewlett Packard 8542A) with a wave length of 280 nm [11].

3.3. Fluidity of cement paste

The cement pastes with two W/C ratios (0.25, 0.30) and two SNF/C ratios (0.25%, 0.50%) were prepared by mixing proper amount of cement with water for 5 min after adding the SNF solution. The addition time of admixture varied from 0 to 60 min. The mixture proportions for the cement pastes are listed in Table 3. The fluidity of the cement paste was determined by the spread diameter on a vibrated spread table.

3.4. Slump of concrete

Concrete with W/C ratio (0.30) and three SNF/C ratios (0.50%, 1.0% and 2.0%) was prepared by mixing proper amount of cement, aggregates with water for 5 min after adding the SNF solution, tempering for 3 min and remixing for 4 min. The addition time of admixture varied from 0 to 60 min. The mixture proportions of concrete are listed in Table 4. The workability of the concrete was determined by the slump value in a slump test. The air content of prepared concrete samples is about 1.5–2.0%.

Table 3
Mixture proportions of cement pastes

W/C	0.25	0.25	0.30
[a]Water (g)	275	275	330
Cement (g)	1100	1100	1100
SNF/C (wt%)	0.25	0.50	0.25
[b]Admixture (g)	2.75	5.50	2.75

[a] Including admixtures.
[b] Based on 100% solid content.

Table 4
Mixture proportions of concrete (W/C = 0.3)

Water[a] (kg/m^3)	198	198	198
Cement (kg/m^3)	586	586	586
Fine aggregate (kg/m^3)	800	800	800
Coarse aggregate (kg/m^3)	663	663	663
SNF/C (wt%)	0.50	1.0	2.0
Admixture[b] (kg/m^3)	2.93	5.86	11.7

[a] Including admixtures.
[b] Based on 100% solid content.

4. Results and discussion

4.1. Adsorption of SNF on cement particles

The adsorption behavior of SNF in cement for different initial concentrations was studied. Fig. 1 shows that the SNF concentration decreases rapidly in the first 5 min after its addition into all cement slurries. Within this period, SNF concentrations in the slurries are relatively higher, and the surfaces of cement particles are more active and also contain more empty sites. Therefore, the adsorption rate is relatively high. After 5 min, the SNF concentration decreases more slowly, and approaches a constant equilibrium value gradually. The adsorption behavior is found to be similar for different addition times. However, the equilibrium SNF concentration is higher for a delayed addition. In addition, the results in Fig. 2 with higher initial admixture concentration indicate similar patterns as those in Fig. 1.

From the results in the previous two figures, the SNF concentration was found to reach a constant value when adsorption time $\geqslant$ 10 min for most cases. However, for the case when the addition time = 0 min, it takes longer adsorption time to achieve an equilibrium state. Therefore, the equilibrium time was taken as 20 min. Table 5 summarizes the experimental results. It is seen from this table that the M value increases with the initial SNF concentration or decreases with longer addition time.

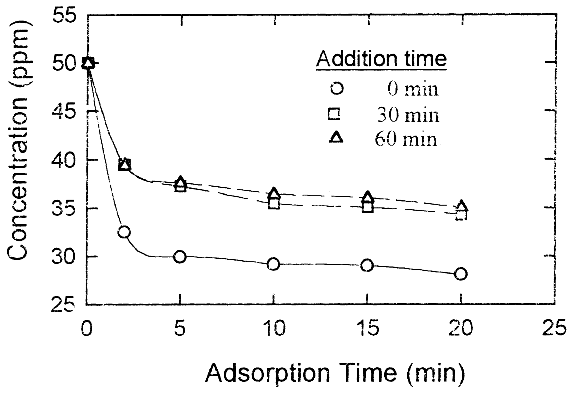

Fig. 1. Effect of addition time on SNF adsorption ($[SNF]_i = 50$ ppm).

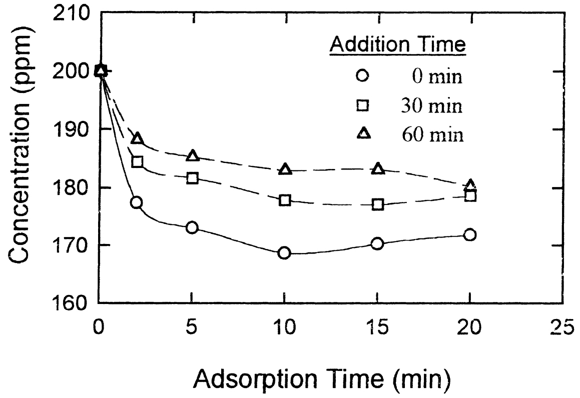

Fig. 2. Effect of addition time on SNF adsorption ($[\mathrm{SNF}]_i$ = 200 ppm).

Table 5
Relationship between the initial concentration ($[\mathrm{SNF}]_i$), concentration at equilibrium ([SNF]eq) and the amount adsorbed of admixture (M) at different addition times

Addition time (min)	$[\mathrm{SNF}]_i$ (ppm)	[SNF]eq (ppm)	M (g)
0	50	28.1	0.0131
0	100	74.6	0.0152
0	200	172	0.0169
0	300	271	0.0171
5	50	31.9	0.0108
5	100	78.7	0.0128
5	200	75.4	0.0148
10	50	34.2	0.00949
10	100	81.6	0.0110
10	200	176.1	0.0143
30	50	34.3	0.00942
30	100	80.9	0.0115
30	200	179	0.0128
30	300	277	0.0138
60	50	35.1	0.00899
60	100	82.3	0.0107
60	200	180	0.0119

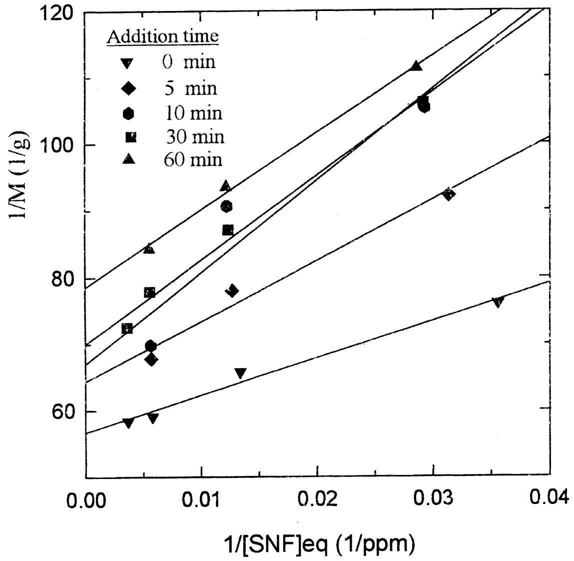

Fig. 3. Relationship between $1/M$ and 1/[SNF]eq.

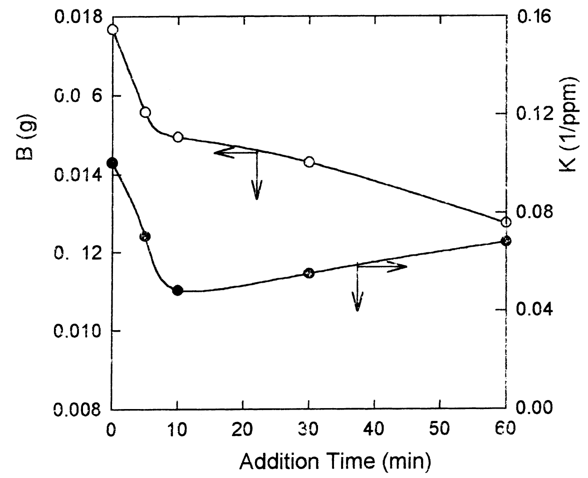

Fig. 4. Relationship between B, K and addition time.

Fig. 3 shows the relationship between $1/M$ and the reverse of the SNF concentration at equilibrium (1/[SNF]eq). It is clear that the M value increases with [SNF]eq. Furthermore, a linear relationship exists between $1/M$ and 1/[SNF]eq. This implies that the adsorption behavior of SNF indeed follows the Langmuir isothermal adsorption model, and only a monolayer of SNF molecules was adsorbed on cement particles [7,11]. Finally, the saturated adsorbed amount of SNF (B) and the equilibrium constant (K) could be determined based on (3) from the intercept and the slope of each line in Fig. 3.

Fig. 4 shows the effect of addition time on the B and K values. Clearly the B value decreases with addition time, since the number of adsorbed sites is decreased with the degree of cement hydration due to a change in composition and electrokinetic characteristics of the cement surface [2]. Moreover, the rate decrease is rapid over the period of 0–10 min. It is known that sulfate ions, coming from the dissolution of gypsum, play an important role on the early hydration rate of cement through the reaction with C_3A. Sulfonated superplasticizers such as SNF, have also been shown to interact with aluminate phases, competing with sulfate ions. Thus, the rapid rate decrease in the early period can be attributed to a strong adsorption of SNF onto the tricalcium aluminate phase [9,17]. Finally, as addition time is increased, the K value first decreases, reaches a minimum value at about 10 min and then increases.

It should be noted that both *B* and *K* values show a transition with addition time in Fig. 4. This seems to be related to a change of the SNF adsorption behavior on cement particles. The main components of Portland cement include tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminum ferrite. For the cement we used, two exothermal peaks of reaction were observed, as obtained from measuring the rate of heat evolution of a cement paste (W/C = 0.4) during the hydration reaction. The early reaction starts from the hydration of tricalcium silicate and tricalcium aluminate with water [18]. The corresponding first heat peak occurs at about 0–15 min. During this period, cement first dissolves in water, releases Ca^{2+} and some OH^- ions into solution, and then undergoes hydration. Meanwhile, Ca^{2+} ions chemisorb on the cement surface and make it positively charged [19]. This facilitates the adsorption of the negative charge-containing admixture molecules, and this adsorption behavior is classified as chemical adsorption. As time elapses, hydrated cement products, such as C–S–H gel and ettringite, are gradually formed and the number of positive charges on the cement surface decreases [20]. In addition, the concentration of SNF in the solution is progressively decreased as some adsorbed polymers become entrapped in hydration products. This causes a decrease in both *K* and *B* values. When the initial hydrolysis ends, the dormant period starts and it lasts for about 4 h. Then the second exothermal peak occurs at about 4 h 8 min. At this period, many hydrated cement products are formed and cover the particle surface. Concurrently, the ionic strength in the solution is increased. In contrast to the early reaction, this adsorption behavior would be classified as physical adsorption. Both *K* and *B* values for physical adsorption should be lower than those for chemical adsorption. Therefore, the transition points in Fig. 4 would be an indication of a change from chemical adsorption to physical adsorption.

4.2. Workability of cementitious materials

Fig. 5 shows the effects of addition time on the fluidity of cement pastes. The paste (W/C = 0.3) without superplasticizers shows a spread diameter of about 20 cm. The fluidity of the cement paste would be greatly improved when SNF was added and adsorbed on the cement particles to cause a better deflocculating and dispersion action [20]. In general, the fluidity in Fig. 5 was observed to decrease with longer addition time, but to increase with the amount of SNF. It can be noted that a transition point at about 10 min occurs in the three curves of this figure, indicating that the fluidity decreases more quickly when the addition time is more than 10 min. Chiocchio and Paolini [7] have previously studied the effect of time for adding either SNF or SMF to cement pastes. They also concludes that the maximum workability of cement pastes is obtained for both admixtures when the addition time corresponds to the beginning of the dormant period of the cement hydration without admixture. Furthermore, the fluidity of cement pastes with a slightly delayed addition (addition time = 2 min) was observed to be slightly higher than that for immediate addition. According to Uchikawa et al. [8] the improvement of fluidity of cement paste by later addition is caused by a significant reduction of amount of the admixture adsorbed to tricalcium aluminate phase. Also the density of admixture adsorbed on the uppermost surface of the adsorbed layer in later addition is higher than in simultaneous addition.

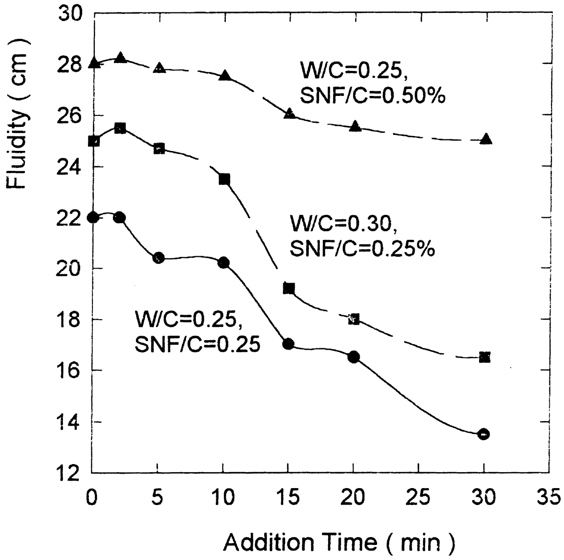

Fig. 5. Effect of addition time on fluidity of cement pastes.

Fig. 6 shows the effects of addition time on the slump of concrete. It can be noted that higher slump values were obtained for concrete with W/C = 0.3 and SNF/C = 2%, and this value is almost constant or is independent of the addition time, which is similar to the results of Kasami et al. [6]. The slump value decreases with addition time for concrete with W/C = 0.3 and lower SNF/C ratio, similar to the results of Hewlett [5]. This indicates that the influence of addition time on concrete workability partly depends on mixture proportions. Again, a transition point can be observed in Fig. 6, at about 10–15 min, which is slightly longer than the time for cement pastes. This could be related to the diluting effect of the aggregates. In other words, for a higher slump value or a better workability of fresh concrete, SNF should be added within the first 15 min, which corresponds to the beginning of the dormant period of the cement hydration. Since the transition points found in Figs. 4–6 all occur at about the same period (10–15 min), it is indicated that a strong relationship does exist

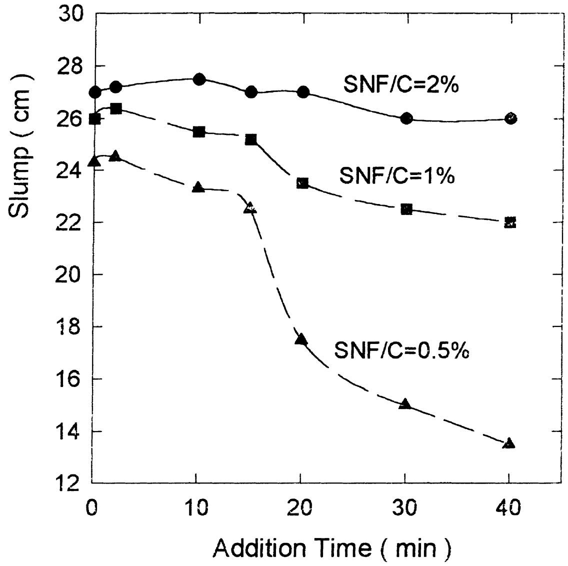

Fig. 6. Effect of addition time on slump of concrete (W/C = 0.30).

between the adsorption behavior of superplasticizers and their dispersing effects on cementitious materials.

5. Conclusion

The influence of addition time of an SNF superplasticizer on the adsorption behavior of type I Portland cement and on the concrete workability was studied. It was found that the adsorption behavior of SNF on cement particles follows the Langmuir isothermal adsorption model. The saturated adsorption amount of SNF decreases sharply with the addition time at the beginning and then slows down. In contrast, the fluidity of cement pastes and the slump of concrete decreases slightly with the addition time in early time and then falls off abruptly. A close relationship apparently exists between the SNF adsorption behavior on cement particles and the workability of cementitious materials because the transition points in both cases were found and appeared to be the same (10–15 min), which corresponds to the beginning of the dormant period of the cement hydration. This suggests that the proper addition time of SNF in concrete should be in this period.

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