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The adsorption behavior of PNS superplasticizer and its relation to fluidity of cement paste

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Abstract

The adsorption behavior of a polynaphthalenesulfonate (PNS) superplasticizer and its relation to the fluidity of cement paste has been investigated for six cements at a given dosage of PNS superplasticizer. The results show that incompatible cements have a higher adsorption capacity of PNS superplasticizer because of a lack of soluble alkali sulfates. There is an inverse relationship between the amount of PNS adsorbed and the mini-slump area value of the cement pastes at 30 min, that is, the higher the amount of PNS adsorbed, the lower the initial slump value, and the higher the slump loss. The addition of some Na_2SO_4 contributes to increase the slump area by reducing the amount of PNS adsorbed. Moreover, it has been found that additional calcium sulfate does not prevent the adsorption of PNS on cement particles as sodium sulfate does in cement pastes having W/C = 0.35. The contribution of alkali sulfate on dispersing mechanism of PNS superplasticized cement pastes is explained in relation with initial slump and its loss. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: PNS superplasticizer; Alkali sulfate; Dispersing mechanism; Adsorption

It is broadly acknowledged that the fluidity of cement pastes usually increases when the dosage of superplasticizer increases. Collepardi et al. [1] explained this phenomenon in this way: the higher the polynaphthalenesulfonate (PNS) dosage, the higher the amount of PNS adsorbed on cement particles, and the higher the fluidity of cement pastes. This phenomenon was based on the fact that PNS adsorption can convey a net negative electrical charge to the surface of cement particles, as well as short-range steric hindrance, inducing repulsive forces between neighboring cement particles, thereby causing increased dispersion.

Results presented by Daimon and Roy [2,3] confirmed the electrostatic repulsive forces induced by superplasticizer. It has been shown that the addition of PNS superplasticizer increases the negative zeta potential of cement particles in pastes, causing larger repulsive forces between cement particles. On the other hand, Banfill [4] suggested that the steric repulsive forces induced by superplasticizer molecules are equally important as the dispersing mechanism. These results were supported by some researchers [5–8] since high-molecular weight polymers lead to additional short-range repulsive forces, while low-molecular weight polymers usually exhibit weak water reduction and low paste fluidity properties. More recently, the relative importance of electrostatic and steric effect has been considered in particle–particle repulsion by Uchikawa et al. [9]. They concluded that electrostatic forces play a major role in the dispersion mechanism for PNS superplasticizer while steric forces are critical for a copolymer of acrylic acid with acrylic ester superplasticizer. However, in discussion of these two dispersing mechanisms, it is generally assumed that superplasticizer molecules have to be adsorbed on the cement particles in order to develop electrostatic and steric repulsive forces.

The relationship between the adsorption of an admixture and its effect on the fluidity of various types of cement paste, was studied by Uchikawa [10]. In the cement pastes containing a given dosage of PNS superplasticizer, they found that the lower the amount of admixture adsorbed by cement, the larger the paste flow. It has also been shown by Jolicoeur et al. [11] that the slump, and slump retention, are related to the amount of "free" or available excess superplasticizer in the interstitial solution of the fresh paste. These results were confirmed by Yamada et al. [12].

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Although equilibrium is never established in this adsorption process, an increase of the PNS dosage leads to an increase of both the amounts of PNS adsorbed and the amounts of PNS in the interstitial solution (free). However, because PNS adsorption is initially irreversible up to a certain "saturation dosage" (i.e., saturation of surface reaction sites), there exists no simple model to predict the evolution of PNS_{free} as a function of PNS_{total} dosage and time.

In this study, the relationship between the fluidity of the cement pastes and the amount of PNS adsorbed was investigated with only one dosage of superplasticizer for each given cement and added Na_2SO_4.

1. Experimental

1.1. Materials

Six commercial cements and a PNS superplasticizer were used for this investigation. Table 1 presents the chemical and Bogue composition of these cements as well as their fineness. Their total Na_2O soluble equivalent contents range from 0.06% for cement C6 to 0.72% for cement C4. The characteristics of the PNS superplasticizer were reported in detail in a previous paper [13]. Sodium sulfate was premixed with the cement used before being mixed with water. Paste mixing procedure and method of mini-slump measurement were described in a previous paper [13]; the dosage of sodium sulfate is expressed as a percentage of cement.

1.2. Adsorption measurement

PNS adsorption on the surface of cement particles was evaluated by measuring the amount of PNS in the solution extracted from fresh cement paste samples; the results were expressed as a percentage (amount of PNS adsorbed relative to the total amount of PNS added). The solution was obtained by pressure filtering system. A nitrogen gas pressure of 345 kPa (50 psi) was applied on the paste placed over 0.45 μm pore diameter filter. The original filtered solution was diluted with deionized water to obtain a suitable PNS concentration. The PNS concentration in solution was measured by a Hewlett-Packard diode array UV–visible spectrometer. The UV spectrum of a PNS superplasticizer consists of two peaks, an intense absorption peak at approximately 230 nm and a much weaker peak in the range between 276 and 294 nm. In this study, we measured the PNS absorbance at the weaker peak because the extinction coefficient of a monomer naphthalene sulfonate and that of the polymer at 230 nm are quite different, on the other hand, the extinction coefficient in the range between 276 and 294 nm does not vary with different polymerization degrees of the PNS [14,15]. Samples were taken at different times (2, 5, 15, and 30 min). The results were found to be reproducible and the precision of the method is of the order of ±2.0% (at a 95% confidence level).

Table 1
Chemical and phase composition of six cements used
Measuring method of soluble alkalies is stated in Ref. [13].

Chemical composition (%)	C1	C2	C3	C4	C5	C6
SiO_2	21.39	21.53	20.39	21	19.93	21.14
Al_2O_3	3.74	3.52	5.02	4.2	4.76	5.23
Fe_2O_3	3.96	4.11	2.2	3.1	3.23	2.04
CaO	65.43	63.69	62.3	61.5	64.95	64.6
MgO	1.4	2.18	2.49	2.6	1.37	2.75
SO_3	1.95	2.85	2.9	3.4	2.67	2.95
K_2O	0.33	0.56	1.05	0.8	0.25	0.21
Na_2O	0.06	0.1	0.22	0.21	0.18	0.18
Na_2O eq.	0.31	0.52	0.92	0.74	0.35	0.31
Soluble alkalies	0.19	0.41	0.57	0.72	0.07	0.06
CaO free	1.82	0.81		0.5		
C_3S	73	66	53	51	69	56
C_2S	6	12	18	20	5	17
C_3A	3	2	10	6	7	11
C_4AF	12	13	7	9	10	6
Blaine (m^2/kg)	420	480	370	410	380	380

1.3. Measurement of sulfate ion concentration in solution

The total sulfur (from the sulfate ions in cement and the sulfonate ions of the PNS) concentration in solution in fresh cement pastes was measured using ICP (inductively coupled plasma) spectrometry. The measurements were carried out 30 min after mixing. The original filtrate solution obtained by the system described above was diluted to 1:150 with 5% HCl. The sulfate ion concentration from the cement was calculated by subtracting the sulfur content in the PNS superplasticizer from the total sulfur concentration.

1.4. Evaluation of ettringite formation in cement pastes

The measurement of the amount of ettringite formed at 30 min in cement pastes was performed by Lafarge Canada using the DSC (different scanning calorimeter, model 821E Mettler). The method used by Lafarge is best suited for relative (rather than absolute) measurements. A sample of cement paste is de-watered by air suction and then is placed in excess isopropyl alcohol in order to stop the hydration reaction. The sample is submitted again to suction drying and subsequently dried in a fume hood at room temperature. A sample of about 30–35 mg is placed and sealed in a crucible with a lid having two pinholes. According to experience with DSC analyses by Lafarge researchers, these pinholes allow to control the vapor pressure over the sample in a such a way that gypsum loses its water molecules at a higher temperature. Therefore, the procedure thus contributes to separate the peak of ettringite from the peak of gypsum. A heating rate of 3°C/min or 5°C/min is used. In such a condition, the results show that the peak of ettringite is well separated from the peak of gypsum. The amount of ettringite formed is measured in the temperature range of 45–125°C and is calculated by integration of the peak area, relative to the peak area (J/g) observed when pure ettringite is dehydrated in an unhydrated cement powder matrix.

2. Results and discussion

2.1. Compatibility between cements and PNS and relation to adsorption behavior

In a previous paper [13], it was found that cements C1, C5, and C6 containing a low amount of soluble alkali content were not compatible with PNS superplasticizer, while cements C2, C3, and C4 containing a high amount of soluble alkalis were compatible as shown by the Marsh cone test. This was also confirmed by the mini-slump test as shown in Fig. 1. These results show that the pastes made with cements C2, C3, and C4 including a given dosage of PNS superplasticizer have a high initial mini-slump spread area value and maintain this high value for 90 min. On the contrary, pastes made with cement C1 present a high initial slump, but a rapid slump loss. In the case of cement C5, the initial slump is maintained for about 15 min, but then decreases rapidly. The paste made with cement C6 has a relatively low slump even at 2 min although the dosage of superplasticizer is high 1.0%. These observations confirm that cements C1, C5, and C6 are not compatible with the PNS superplasticizer used.

The amount of PNS adsorbed by the six cements as a function of time is presented in Fig. 2. It is found that the amount of PNS adsorbed in cements C1 and C6 has already reached 75% at 2 min and about 90% at 30 min. In the case of cement C5, the initial amount of PNS adsorbed is as low as in the case of the compatible cements C2, C3, and C4, but later on, this amount dramatically increases as a function of time. It is also observed that the three compatible cements adsorb low amounts of PNS up to 30 min. It is interesting to note (Fig. 3) the inverse relationship between the amount of PNS adsorbed and the mini-slump value of cement pastes at 30 min: the higher the amount of PNS adsorbed, the lower the slump value at 30 min. These results agree with previous research [10–12]. The uptake rate of PNS by cement particles seems to be related to the mineral composition of the cement used, especially the amounts of C_3A, C_4AF, and C_3S [16]. In this study, however, it is clearly seen that the incompatible cements containing a low amount of soluble alkalis have a tendency to adsorb a high amount of PNS superplasticizer at 30 min, while the compatible cements containing a high amount of soluble alkalis do not, leaving a

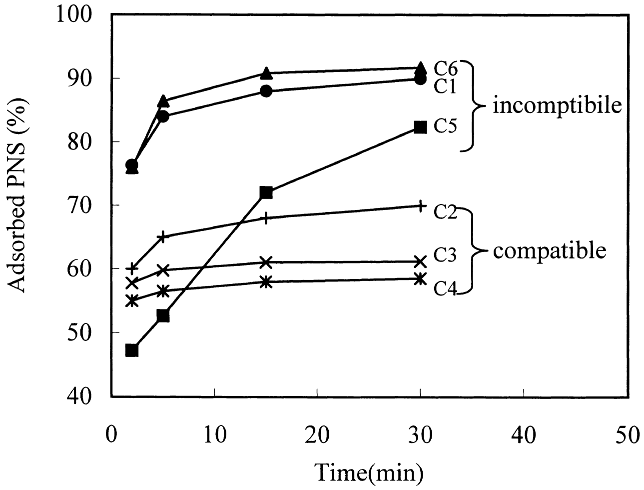

Fig. 2. The percentage of PNS adsorbed on cement particles as a function of hydration time at W/C = 0.35.

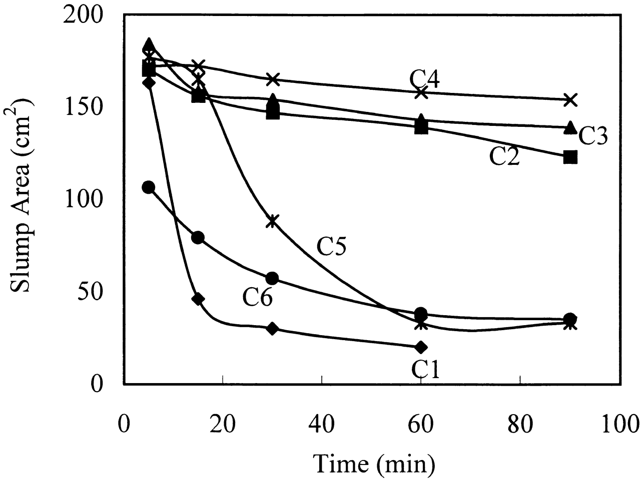

Fig. 1. The fluidity of cement pastes as a function of hydration time. The dosage of PNS superplasticizer: 0.6% for C2, C3, C4, and C5, 1.0% for C1 and C6.

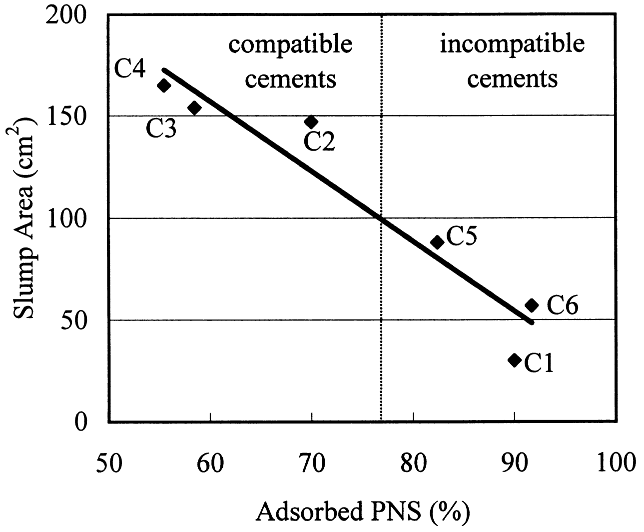

Fig. 3. The relationship between the percentage of PNS adsorbed and mini-slump area at 30 min.

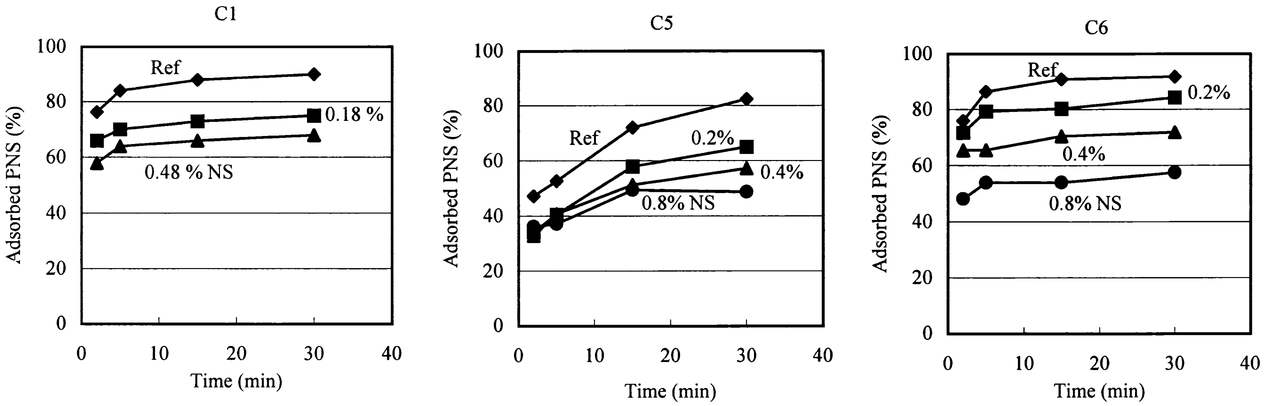

Fig. 4. The percentage of PNS adsorbed as a function of hydration time after the addition of Na_2SO_4 (NS).

higher amount of PNS superplasticizer in solution. Therefore, the soluble alkali content in cement appears as an important factor on the adsorption behavior of PNS superplasticizer.

2.2. The effect of Na_2SO_4 and calcium sulfate addition on PNS adsorption and on the fluidity of cement pastes

In a previous paper [13], it was found that the soluble alkali content is a key parameter when studying the compatibility between a cement and a superplasticizer, and that the addition of a small amount of sodium sulfate can reduce the slump loss of a superplasticized cement paste. It was also found that the slump loss was minimal for an optimum content of soluble alkalis. In the present work, the effect of sodium sulfate addition on the PNS adsorption as a function of time was investigated. It is clearly seen in Fig. 4 that the percentage of PNS adsorbed is reduced when the amount of added sodium sulfate increases. In the case of cements C1 and C6, the initial amount (2 min) of PNS adsorbed is reduced when the amount of sodium sulfate is increased. In the case of C5 cement, the addition of sodium sulfate does not affect the initial amount of PNS adsorbed, but has a significant influence on PNS adsorption at 30 min. These results show that the initial adsorption remains low but that it increases with time for C5.

The relationship between the percentage of PNS adsorbed at 30 min and the slump area of the cement pastes is presented in Fig. 5. It is noteworthy that the addition of Na_2SO_4 contributes to increase the slump area by reducing the amount of PNS adsorbed: the role of alkali sulfate on the dispersion mechanism of PNS superplasticized cement pastes will be discussed later.

It has earlier been found that the addition of gypsum, or hemihydrate, to the three incompatible cements C1, C5, and C6 is not as effective as the addition of Na_2SO_4 on reducing the slump loss [13]. The effect of calcium sulfate on PNS adsorption has been investigated in this study. As shown in Fig. 6, calcium sulfate does not prevent the adsorption of PNS on cement particles to the same extent as sodium sulfate; this is presumably the result of the lower solubility of $CaSO_4$ relative to $(Na,K)SO_4$ and the low amount of water available at W/C = 0.35.

Nawa and Eguchi [16] studied the adsorption isotherms of PNS on synthetic C_3A, C_4AF, and C_3S. They pointed out that sulfate ions originating from gypsum or sodium sulfate

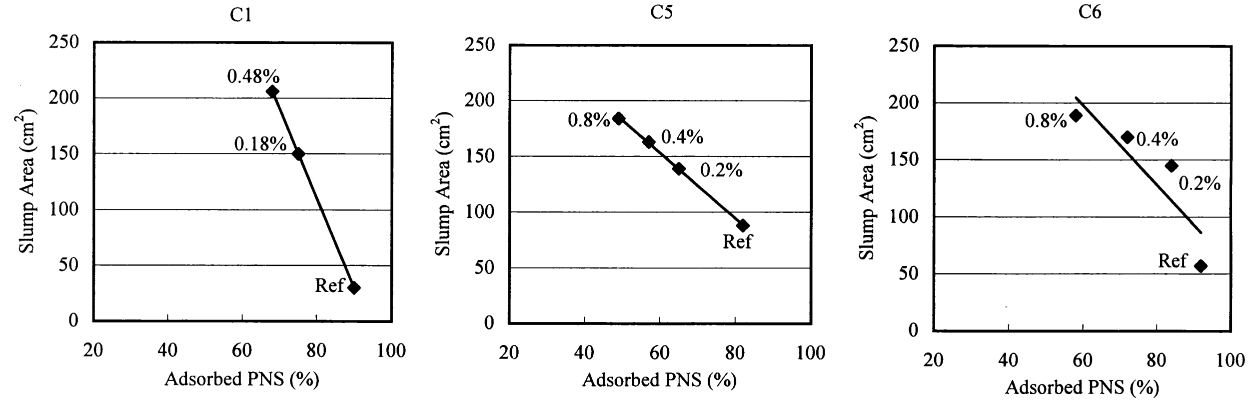

Fig. 5. The relationship between the percentage of PNS adsorbed and mini-slump area at 30 min for cement pastes with various Na_2SO_4 contents.

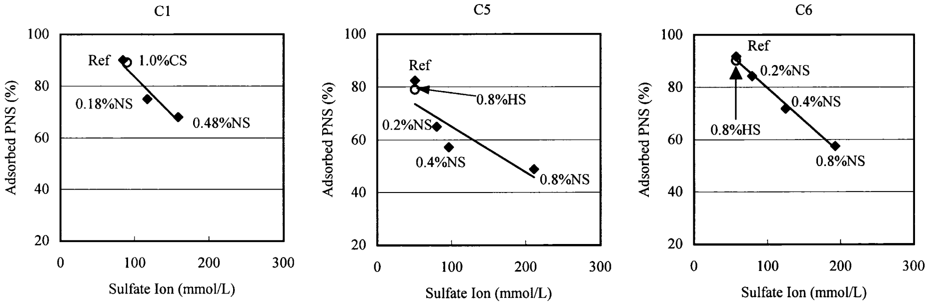

Fig. 6. The relationship between the percentage of PNS adsorbed and the concentration of sulfate ions at 30 min. NS: Na_2SO_4, CS: $CaSO_4$ $2H_2O$, HS: $CaSO_4$ $1/2H_2O$.

inhibited the adsorption of PNS onto C_3A and C_4AF, and enhanced it on C_3S in a solution having a water/solid ratio of 5.0. Hemihydrate was more effective in reducing the adsorption of PNS, especially on C_4AF as compared to sodium sulfate at the same dosage. However, as shown in Fig. 6, additional calcium sulfate does not prevent the adsorption of PNS on cement particles in comparison with sodium sulfate. These results agree with Bonen and Sarkar [17] indicating that the fluidity of the superplasticized cement paste at W/C = 0.35 was not increased by the addition of gypsum up to 7%, while at W/C = 0.50, the fluidity was improved.

2.3. Effect of Na_2SO_4 and calcium sulfate addition on ettringite formation

Uchikawa [10] measured the amount of four different superplasticizers adsorbed on synthetic cement compounds and cement hydrates. Their results showed that the amount of PNS adsorbed on C_3A and C_4AF is greater than that on ettringite. That is, when a 100-mg/g PNS was added, the amount of PNS adsorbed on C_3A, C_4AF and ettringite is 94.3, 91.5, and 37.4 mg/g, respectively. Therefore, it was assumed that when sodium sulfate is added to a cement paste, it could promote the early formation of some ettringite with C_3A by providing SO_4^{2-} ions and therefore contribute to reduce the amount of PNS adsorbed.

The amount of ettringite was measured by DSC at 30 min for cements C5 and C6 and the results are presented in Fig. 7. Contrary to our assumption, the amount of ettringite was not found to increase significantly upon adding either some sodium sulfate or hemihydrate. However, when comparing cement pastes without and with PNS superplasticizer (C + W and reference C + W + PNS) in Fig. 7, there is evidence that PNS itself increases the amount of ettringite formed. The amount of ettringite formed increases with increasing C_3A content (cement C5 has 7% of C_3A and cement C6 has 11% of C_3A). These results also are in agreement with those of Bonen and Sarkar [17] suggesting that the flow loss does not correspond to the amount of ettringite formed.

2.4. The role of alkali sulfate on dispersion mechanism of superplasticized cement paste

As previously noted, it is generally acknowledged that the dispersion mechanism in a PNS superplasticized cement paste is the following: the superplasticizer is adsorbed onto cement particles and this adsorption conveys a net negative

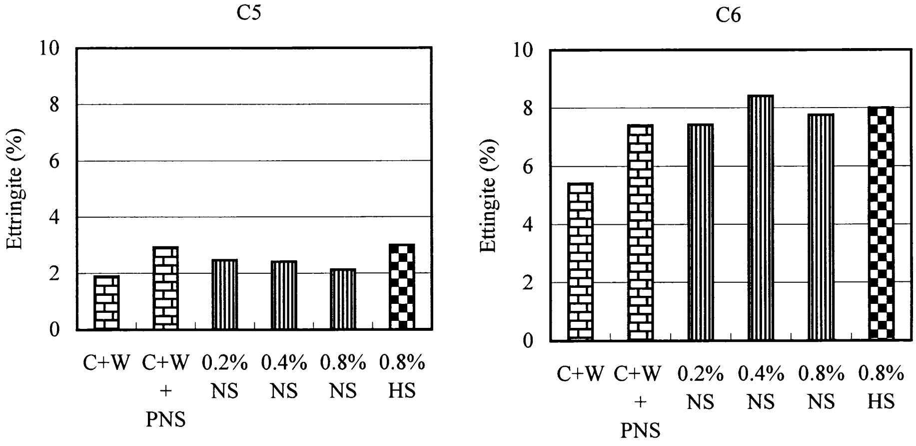

Fig. 7. The effect of the addition of sodium sulfate and hemihydrate on the formation of ettringite at 30 min. Reference C + W + PNS, NS: Na_2SO_4, HS: $CaSO_4$ $1/2H_2O$.

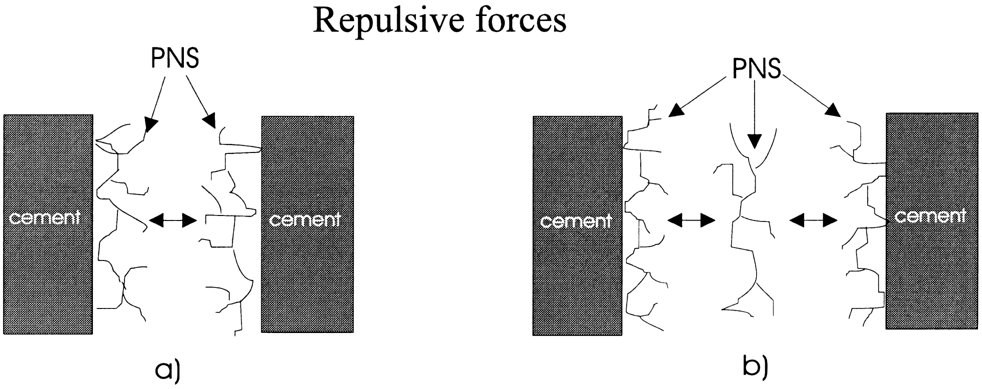

Fig. 8. Repulsive forces, (a) without free PNS, (b) with free PNS in the interstitial solution.

electrical charge to the surface of cement particles resulting in long-range electrostatic repulsive forces and short-range steric repulsive forces between cement particles. These induced repulsive forces contribute to increase the fluidity of cement paste [12]. This explanation indicates that for a given low dosage, the fluidity of cement pastes should increase with the amount of PNS superplasticizer adsorbed on the cement particles. However, the experimental results here indicate the opposite trend, as illustrated in Fig. 3.

On the basis of the present results and data from other published papers [10–12,18], the role of alkali sulfate on dispersion mechanism of superplasticized cement paste is suggested as the following: when a PNS superplasticizer is added to cement pastes containing a low amount of soluble alkali content, most of the PNS added is consumed by the formation of organo-mineral compounds [19] and/or the hydrated products incorporating PNS [20] in 30 min. The PNS molecules "intercalated" into the hydration products cannot contribute to improve the fluidity of cement pastes. However, when sodium sulfate is added in the cement pastes, the sulfate ions dissolved from sodium sulfate inhibit the adsorption of PNS superplasticizer on the aluminate phases by competing with the PNS molecules for adsorption sites (the early PNS adsorption effectively reduces the positive potential of C_3A and C_4AF [18]). The competition between PNS and sulfate ions reduces the amount of PNS consumed and thus enables more PNS to remain in solution and/or to be adsorbed on the silicate phases as well. The PNS molecules remaining or "free" PNS, in solution may then act as an additional repulsive barrier between cement particles, further contributing to improve the fluidity of the paste. The repulsive forces between the "free" PNS and adsorbed PNS cement particles are illustrated in Fig. 8. As hydration proceeds, the PNS molecules adsorbed on the solid surface become ineffective due to incorporation into newly formed hydration products. The PNS remaining in solution is then progressively adsorbed onto the newly hydrated surfaces; the continuous supply of PNS molecules maintains the electrostatic and steric repulsive forces to conserve paste fluidity. In the case of incompatible cements, the excessive early PNS adsorption leaves little free PNS molecules for replacing the PNS consumed into the hydration product. In such case, delayed addition of PNS, as often performed in the field, restores the fluidity by reestablishing the supply of free PNS.

3. Conclusion

The three "incompatible" cements containing low amount of soluble alkali have been found to have a tendency to adsorb a high amount of a PNS superplasticizer, while the three "compatible" cements containing high amount of soluble alkali do not, leaving a higher amount of PNS superplasticizer available in solution. For a given cement, it is clearly seen that the PNS adsorption capacity of a cement is strongly influenced by the soluble alkali content. Due to the use of a constant initial PNS dosage, there appears to be an inverse relationship between the amount of PNS adsorbed and the slump area of cement pastes at 30 min, and a direct relation between the amount of PNS adsorbed and the rate of the slump loss.

The addition of Na_2SO_4 to the three incompatible cements contributes to increase the fluidity of the pastes by reducing the amount of PNS adsorbed. The amount of PNS adsorbed for a given cement is independent of the amount of ettringite formation.

The addition of calcium sulfate does not have much effect on the adsorption of PNS on cement particles in cement paste having a water/cement ratio of 0.35. This is because, at low W/C and short times (0–30 min), the bulk of the SO_4^{-2} ions is supplied by the alkali sulfates.

Acknowledgments

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