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Cement and Concrete Research 34 (2004) 839–844

CEMENT AND CONCRETE RESEARCH

The effect of the kind of calcium sulfate in cements on the dispersing ability of poly β-naphthalene sulfonate condensate superplasticizer

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Received 17 March 2003; accepted 22 September 2003

Abstract

Many studies have been carried out to prevent the incompatibility problem between poly β-naphthalene sulfonate condensate superplasticizer (PNS) and cements. Several of them suggested that the effect of SO_4^{2-} concentration on adsorption equilibrium might be more important for the performance of PNS than the effect of ionic strength on electrostatic repulsion. In this study, the influence mechanism of the kind of calcium sulfate in cements on the performance of PNS was analyzed in regards to SO_4^{2-} concentration change with time elapse. It was found that SO_4^{2-} concentration change was affected by two kinds of calcium sulfate, gypsum and hemihydrate. In case of using the cement containing mainly hemihydrate, SO_4^{2-} concentration in the solution phase of cement paste initially after mixing is high; however, it decreases rapidly with time elapse. The adsorbed amount of PNS onto surface of cement particle is limited just after mixing because the SO_4^{2-} concentration is high and increases with decreasing SO_4^{2-} concentration. As a result, the flow loss of cement paste decreases.

Keywords: Adsorption; Cement Paste; Dispersion; Modeling

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1. Introduction

Poly β-naphthalene sulfonate condensate superplasticizer (PNS) is used widely as a dispersant for cement or as a concrete admixture. With superplasticizers, it is possible to control concrete rheology without altering water–cement ratio (W/C) that governs concrete durability and strength. However, not all cement–PNS combinations are compatible because the dispersing performance of PNS is easily affected even by slight differences of cement characteristics from different plants or lots [1–3]. This is a serious problem for concrete works. There are numerous studies investigating cement characteristics that affect the dispersing ability of PNS.

Many studies indicated that the dispersing ability of PNS was due to electrostatic repulsion between cement particles [4,5], and suggested that the electrostatic repulsion was mainly affected by the composition of solution phase [5,6]. However, recent studies showed that the dispersing performance was also dependent on the adsorbed amount of PNS on the surface of hydrated cement [7,8].

The performance of PNS is known to be affected by several cement characteristics, e.g., kinds of calcium sulfate, amounts of alkali sulfate and so on. The well-known effect of alkali sulfate has already been investigated in detail. Several studies have reported the existence of an optimum content of alkali sulfate for the highest flow [5,9] and for avoiding rapid slump loss [9]. These phenomena are thought to be governed by the composition of solution phase [5,6].

Another important phenomenon that should be considered is the absorption of PNS into initial hydrates, which shows no dispersing performance. Only the PNS adsorbed on the hydrates are expected to work as a dispersant. However, it is difficult to estimate the effect of alkali sulfate on the absorption and adsorption of PNS because there is no quantitative method to discriminate between adsorbed PNS onto hydrate and absorbed PNS into hydrate. Recently, the authors proposed that assuming a competitive adsorption of Langmuir type on hydrates for PNS with SO_4^{2-}, adsorbed PNS can be estimated indirectly. This is important for determining the working mechanism of alkali sulfate [10,11].

For the working mechanism of the kind of calcium sulfate, the effect of solution phase composition on the performance of PNS has been discussed [5,6]. However,

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doi:10.1016/j.cemconres.2003.09.022

the effect of adsorbed PNS has not been clarified. Therefore, in this study, the effect of the kind of calcium sulfate on the dispersing ability of PNS are examined in consideration of two factors; the chemical composition of solution phase and adsorbed amount of PNS. The adsorbed amount of PNS per unit surface area was calculated using the equation of competitive adsorption equilibrium between PNS and SO_4^{2-} [10,11]. In this study, the amount of calcium sulfate is assumed to be sufficient to suppress the initial hydration of C_3A. When the amount of calcium sulfate is insufficient, the hydration of C_3A may be affected by the slight difference of it and as a result the performance of PNS can be affected.

2. Experimental procedure

The performance of PNS was evaluated by the fluidity of cement paste. The details of the experimental procedure are shown as follows.

2.1. Materials

In this study, two kinds of ordinary Portland cement from different plants were used. Calcium sulfates found in Japanese Portland cement are mainly gypsum and hemihydrate produced by the dehydration of gypsum during the milling process. Dehydration ratio to hemihydrate is defined by Eq. (1).

$$\text{Dehydration ratio to hemihydrate (mol ratio)} = \frac{\text{Hemihydrate}}{\text{Gypsum} + \text{Hemihydrate}} \qquad (1)$$

In this study, two kinds of cements containing different kinds of calcium sulfate were selected. One is OPC-A containing gypsum mainly (dehydration ratio is 0.31) and the other is OPC-B containing hemihydrate mainly (dehydration ratio is 0.87). Their characteristics are summarized in Table 1.

As explained above, the influence mechanism of the kind of calcium sulfate on the performance of PNS was examined from the viewpoint of competitive adsorption of PNS with SO_4^{2-}. SO_4^{2-} concentration in the solution phase is affected by two cement characteristics. One is calcium sulfate and the other is alkali sulfate. In order to minimize the effect of alkali sulfate, K_2SO_4 was added in order to minimize the difference between two kinds of cement. K_2SO_4 was added in the mixing water at 0.39 mass % to OPC-B.

Commercial PNS was used in this study. The solid content of the PNS was 40 mass %.

2.2. Mixing procedures

Cement paste was made by mixing 800 g of cement and 296 g of water at 20 °C, which gave the W/C of 0.37. The mixing condition was manual mixing for 90 s in accordance with JIS R 5201. The dosage of PNS content was 0.48 mass % of cement as a solid. PNS was added in the mixing water.

2.3. Evaluation of cement paste

Paste flow was measured as an index of fluidity by using a flow table of ASTM C 124-73 and a flow cone specified by JIS R 5201. The spread width of the paste on a flow table was measured after 15 drops. The measurements were carried out at the ages of 5–60 min after mixing.

As explained above, it is important to evaluate the composition of solution phase. The solution phase of cement paste was separated by suction filtering at the ages of 5–60 min after mixing. All filtering process took less than 20 s. The sorption amount of PNS was evaluated by measuring the change in PNS concentration from mixing water to the solution phase of cement paste. PNS concentration in the solution was measured by using ultraviolet light adsorption (Spectrophotometer U-3210, Hitachi, Tokyo, Japan). The molecular weight of one unit of PNS structure including one sulfonic group is 242. Because the dispersing ability of PNS is due to the sulfonic group of PNS [12], the amount of PNS is converted into molecular number of unit structure of PNS by using the molecular weight of 242 in this study.

Ion concentration in the solution phase was measured by ion chromatography (IC-7000, Yokogawa, Tokyo, Japan).

3. Results and discussion

3.1. Effect of the kind of calcium sulfate on the performance of PNS

The fluidity changes of cement paste are shown in Fig. 1. In the case of constant alkali sulfate content, initial flow of OPC-A, 401 mm, was higher than that of OPC-B, 376 mm. However, flow loss of OPC-A was larger than that of OPC-B.

Table 1
Cement characteristics

Cement	Chemical composition/mass %					R_2SO_4/mass %	Dehydration ratio to hemihydrate * /mol ratio	Blaine/ $cm^2\ g^{-1}$
	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3			
OPC-A	63.2	22.0	5.6	3.0	2.3	0.82	0.31	3240
OPC-B	64.0	21.6	5.0	2.9	2.1	0.50	0.87	3230

* Dehydration ratio to hemihydrate = Hemihydrate/Gypsum + Hemihydrate.

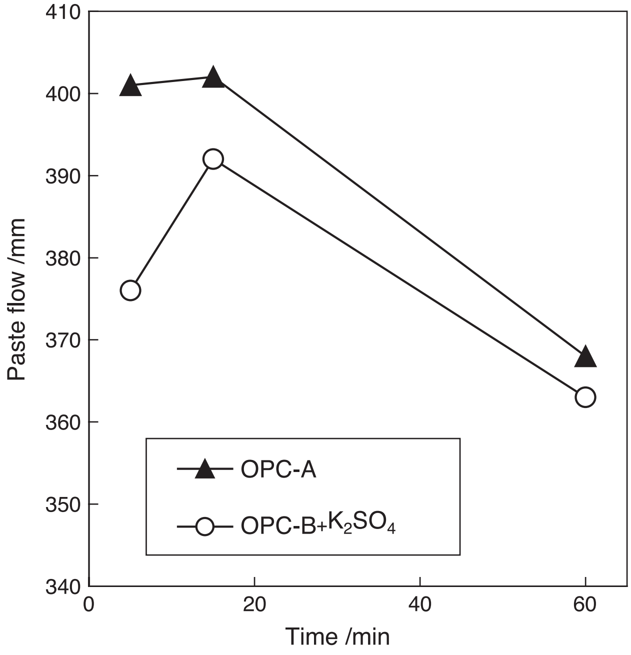

Fig. 1. Change of paste flow with time.

Paste flows at 60 min, which were within 363–368 mm, were almost free from both kinds of calcium sulfate.

The concentration change of SO_4^{2-} with time elapse was measured in order to identify the mechanism of the flow loss.

3.2. Effect of the kind of calcium sulfate on the composition of solution phase

The change of SO_4^{2-} concentration with time elapse in the solution phase of cement paste is shown in Fig. 2. When alkali sulfate was added to OPC-B, SO_4^{2-} concentration increased all through the ages. For example, the initial SO_4^{2-} concentration increased from 109 to 141 mmol/l. The increases in the concentration of SO_4^{2-} were in the range of 31–35 mmol/l for all ages.

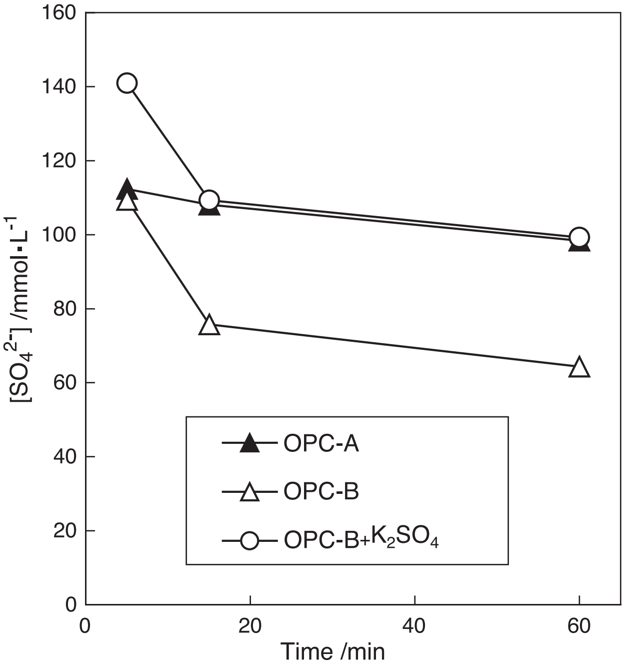

Fig. 2. Concentration change of SO_4^{2-} with time (cement paste).

On the other hand, in the case of constant alkali sulfate content, initial SO_4^{2-} concentration of OPC-B containing hemihydrate mainly, 141 mmol/l, was higher than that of OPC-A containing gypsum mainly, 112 mmol/l. However, SO_4^{2-} concentrations at 60 min were in the range of 98–99 mmol/l and were free from the kinds of calcium sulfate. The effect of the kind of calcium sulfate on SO_4^{2-} concentration in the solution phase of cement paste without PNS had already been reported [13]. The SO_4^{2-} concentration recorded in this study did not fully coincide with the literature data. However, the tendencies of concentration change with time elapse were the same with the literature.

As explained above, there are two cement characteristics that affect SO_4^{2-} concentration in the solution phase of cement paste. One is alkali sulfate that affects the values all through the ages, and the other is the kind of calcium sulfate that affects the initial value only. In the following paragraph, the working mechanisms of these two factors were examined, respectively.

At first, the mechanism of the influence of alkali sulfate on the composition of solution phase was examined. The isotherm of the dissolution equilibrium of $(Na_2SO_4 + K_2SO_4) - CaSO_4{\cdot}2H_2O - Ca(OH)_2$ [14] is shown in Fig. 3. This isotherm shows the composition of the dilute alkali sulfate solution saturated with gypsum and calcium hydroxide. There is a positive relationship between concentration of (Na^+K^+) and $SO_4{}^{2-}$ and a negative relationship between concentration of (Na^+K^+) and Ca^{2+}. The compositions of

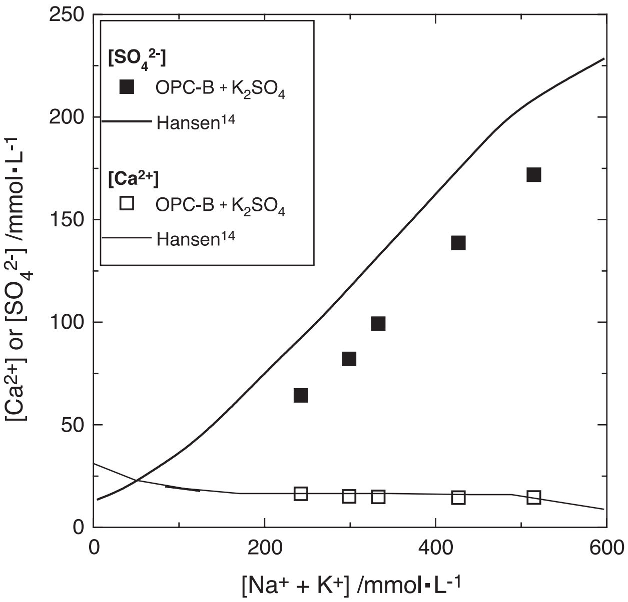

Fig. 3. Relationship between concentrations of Na^+, K^+ and that of Ca^{2+}, SO_4^{2-}.

solution phase of cement paste are also plotted into Fig. 3. The cement pastes were made by mixing OPC-B, mixing water and K_2SO_4. K_2SO_4 was added in the mixing water at 0–0.84 mass % of cement. The composition of solution phase of the paste was measured at 60 min after mixing. The tendencies of concentration change of the paste coincided with the isotherm. This suggests that the dissolution equilibrium showed in Fig. 3 can be applied for the solution phase of cement paste. In Fig. 3, the measurement data of Ca^{2+} concentration were very close to the isotherm. However, SO_4^{2-} concentrations were lower than the isotherm. This difference suggests that the PNS affects the dissolution equilibrium because ionic functional groups are contained in PNS.

Secondly, the influence mechanism of the kind of calcium sulfate on the composition of solution phase was examined. Added to the distilled water and mixed by a magnetic stirrer was 7 mmol/l of gypsum or hemihydrate of reagent grade. The composition of solution phase was measured from 5 to 60 min after mixing. The concentration change of SO_4^{2-} with time elapse is shown in Fig. 4. In the distilled water, initial SO_4^{2-} concentration in hemihydrate paste, 54 mmol/l, was higher than that in gypsum paste, 15 mmol/l. However, SO_4^{2-} concentrations at 60 min were in the range of 14–19 mmol/l and were free from the kinds of calcium sulfate. This suggests that regardless of cement powder addition, the hemihydrate increases the initial SO_4^{2-} concentration and its rate of decrease with time elapse.

3.3. Effect of solution phase composition on the performance of PNS

In order to clarify the effect of SO_4^{2-} concentration on the flow loss by considering the adsorbed amount of PNS, the adsorbed amount of PNS per unit surface area was calculated by using the equation of Langmuir type competitive adsorption.

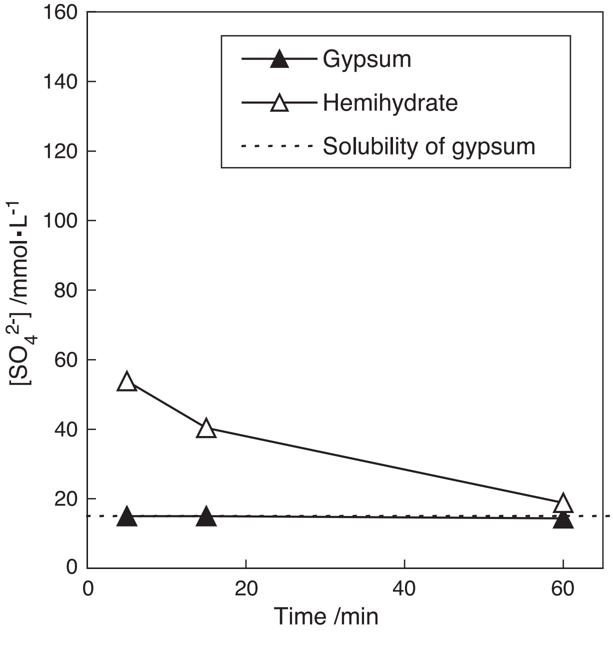

Fig. 4. Concentration change of SO_4^{2-} with time (calcium sulfate paste).

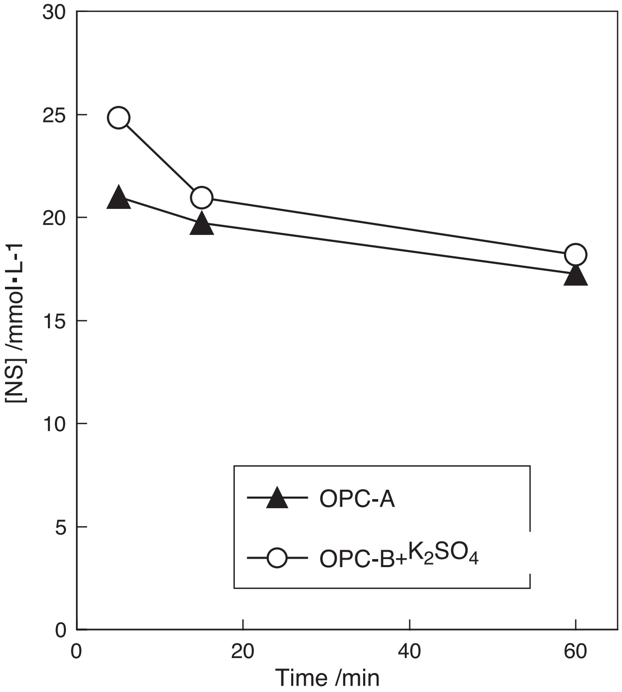

Fig. 5. Concentration change of PNS with time.

Adsorbed amount of PNS per unit surface area can be calculated from PNS and SO_4^{2-} concentrations by using the following equation the authors proposed [10,11,15]. θ_{NS} is the ratio of adsorption sites occupied by PNS to all adsorption sites onto the surface of hydrated cement, which is corresponding to adsorbed amount of PNS per unit surface area. Authors showed that there was a positive linear relationship between θ_{NS} calculated by using Eq. (2) and paste flow [10]. This indicates that the adsorbed amount of PNS per unit surface area is quite important for the dispersing ability of PNS.

$$\theta_{NS} = \frac{1.3[NS]}{1 + 1.3[NS] + 0.027[SO_4^{2-}]} \tag{2}$$

where [NS] is the PNS concentration and $[SO_4^{2-}]$ is the SO_4^{2-} concentration.

From the data of SO_4^{2-} concentration shown in Fig. 1 and the data of PNS concentration shown in Fig. 5, θ_{NS} was calculated by using Eq. (2) and the results are shown in Fig. 6.

In the case of constant alkali sulfate content, the initial θ_{NS} for OPC-A and OPC-B was almost equal. However, the θ_{NS} decrease from 5 to 60 min for OPC-B was less than that for OPC-A. This tendency was almost the same with the flow loss shown in Fig. 1. The relationship between θ_{NS} and paste flow is shown in Fig. 7. Positive relationships between θ_{NS} and paste flow were observed for both OPC-A and OPC-B, respectively. This indicates that the influence of calcium sulfate on flow loss can be explained by the decrease of θ_{NS}.

The decrease of θ_{NS} with time elapse can be explained by the concentration changes of PNS and SO_4^{2-}. OPC-B showed the higher initial PNS concentration than that of OPC-A, and the PNS concentration of OPC-B decreased more rapidly than OPC-A. This indicates that the adsorption of PNS at 5 min was limited because the SO_4^{2-} concentration was relatively high. In addition, the adsorbed amount of PNS increased with time elapse because the SO_4^{2-} concentration decreased more rapidly.

In general, the adsorbed PNS per unit surface area decreases with time elapse because the surface area of the cement particles increases by cement hydration even in this time range. However, a rapid decrease of SO_4^{2-} concentration such as observed in OPC-B affects the adsorption equilibrium to change it to more adsorbed side. As a result, the flow loss of cement paste can be reduced in some degree.

For initial fluidity, the paste flows were different, even θ_{NS} values were the same for two kinds of cement. Particle distribution is known to affect paste flow [16]. This suggests that there is a possibility that the paste flow cannot be explained fully by Eq. (2) because the effect of particle size distribution is not considered in the equation.

As mentioned above, the dispersing performance of PNS is affected by the adsorption equilibrium in the solution phase of cement paste. By considering adsorption equilibrium, it is possible to explain the effect of several factors on the dispersing ability of PNS, i.e., W/C, PNS dosage, early hydration and so on. W/C directly affects on the ion concentration of solution phase. PNS dosage affects the adsorption equilibrium because the ionic functional group is contained in PNS. Early hydration affects the adsorption equilibrium because the total number of adsorption site is proportional to the surface area of cement particle that changes with early hydration. Several studies indicated that optimizing alkali sulfate content and increasing the PNS dosage were effective for delaying slump loss [17]. This study suggests that it is necessary to consider the adsorption equilibrium when discussing these slump loss problems.

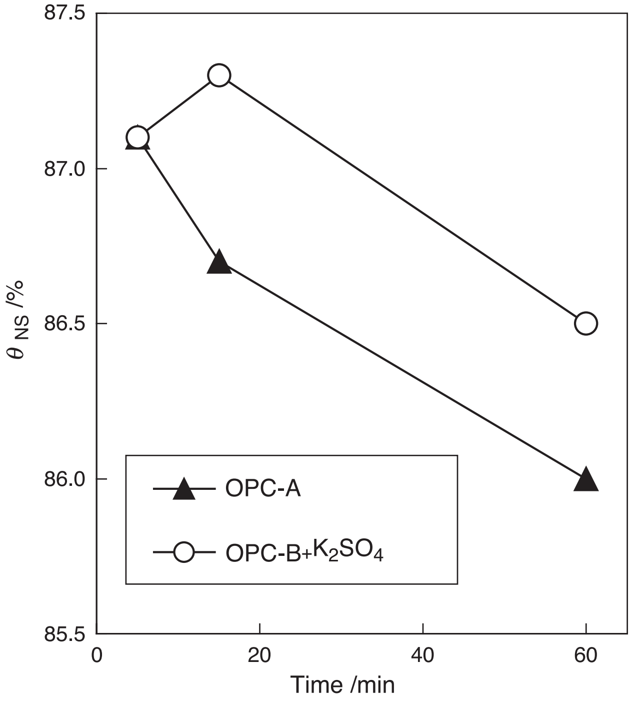

Fig. 6. Change of θ_{NS} with time.

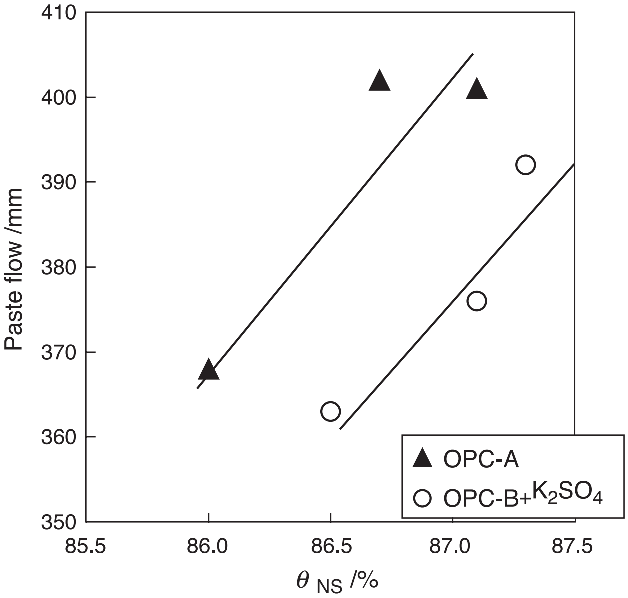

Fig. 7. Relationship between θ_{NS} and paste flow.

4. Conclusions

It is problematic that not all cement–PNS combination is compatible. In this study, the influence of the kind of calcium sulfate on the dispersing ability of PNS was examined by measuring paste flow.

1. The kind of calcium sulfates influences flow loss of cement paste. Flow loss of cement paste is lower when cement containing a higher ratio of hemihydrate as compared to gypsum is used. The mechanism was investigated, considering composition of solution phase and amount of adsorbed PNS per unit surface area. As a result, the following are clarified.
2. Alkali sulfate affects the SO_4^{2-} concentration all through the ages. On the other hand, the kind of calcium sulfate affects the initial value only. When the cement containing hemihydrate mainly is used, initial SO_4^{2-} concentration is higher; however, it decreases rapidly with time elapse.
3. The adsorbed amount of PNS can be calculated by assuming the Langmuir type competitive adsorption of PNS with SO_4^{2-} onto the surface of hydrated cement

particle. From this calculation, it was found that the difference in flow loss between two cement containing different kinds of calcium sulfate could be explained by the effect of SO_4^{2-} concentration on the adsorbed amount of PNS. When the cement containing mainly hemihydrate is used, a rapid decrease of SO_4^{2-} concentration with time elapse affects the adsorption equilibrium. Adsorbed PNS increases as SO_4^{2-} concentration is decreased. As a result, the flow loss of cement paste becomes less.

Acknowledgements

The authors would like to thank the late Dr. Goto of Taiheiyo Consultant for his invaluable advices and helpful suggestions.

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