- Technical Paper -

KINETICS OF WATER ABSORPTION AND DESORPTION OF SUPERABSORBENT POLYMERS AND ITS EFFECT ON PLASTIC VISCOSITY OF CEMENT PASTE AT EARLY AGE

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ABSTRACT

Superabsorbent polymers (SAP) are hydrogels capable of absorbing water, and expected to apply widely to concrete as additives. This study addresses the kinetics of water uptake and release of SAP and the rheologial behavior of fresh cement pastes with SAP. It is suggested that similar variation tendency of absorption capacities of SAP could be obtained by the two measurement techniques. The greater the kinetics of the liquid uptake, the rapider the kinetics of the liquid release. The addition of SAP affects the plastic viscosity, due to supplement of water to alleviate internal friction.

Keywords: superabsorbent polymer, absorption capacity, plastic viscosity, measurement techniques

1. INTRODUCTION

Great advances in concrete technology have been made in recent decades, especially in the use of new chemical additives. Since Jensen an Hansen[1] used superabsorbent polymer (SAP) as additives in concrete, SAP has evolved as multifunctional admixtures for internal curing to mitigate autogenous shrinkage in high-performance concrete with low water to cement ratios. It significantly reduces the potential crack formation caused by self-desiccation[2]. Nowadays, apart from the usage as internal curing additives, new application of SAP to concrete has been of great interest, especially as additives for water control such as rheology modification.

The kinetics of water uptake and release of SAP are key aspects in the SAP technology in terms of their practical applications to cement-based materials. SAPs are a group of polymeric materials that have the ability to absorb a significant amount of water from the surroundings and to retain water within their structure without dissolving[1]. Driven by internal relative humidity (IRH) changes and osmotic pressure of pore solution of concrete, dry SAP particles start to swell upon contact with water. Then the water is released from saturated SAP mainly due to osmotic pressure, which results from the relative high concentration of ions within the SAP's polymer network compared to the external environment[3]. As internal curing reservoirs, SAP addition affects fresh properties of cement-based materials since the water released from SAP can be regarded as internal bleed water. Even if the porosity of cement-based materials with SAP will be higher due to the cavities left by SAP particles, it should be noted that water entrainment with SAP increases the degree of hydration, in a manner similar to increasing the effective water to cement ratio[4]. In addition, the incorporation of SAP is effective in reducing the internal humidity decrease due to the water release from SAP. Mechtcherine et al.[5] have shown that the major factor that governs the rheological properties of fresh mortar is the distinct kinetics of water uptake inherent in the SAP samples, as governed by their particular chemical structures.

The water absorption capacity of SAP gives quantitative expression on the kinetics of water uptake and release of SAP. The measurement techniques usually used for determining absorption capacity include gravimetric and volumetric measurements. The tea bag method is a representative of gravimetric techniques to give a fast response of water absorption capacity of SAP. The absorption capacity evaluated by the tea bag method is founded on the mass of dry SAP in relation to the mass gain of the filled tea bag after it is removed from solution and drop off excess water by gravity. However, this method does not represent the SAP in concrete at early age. As mentioned above, releasing water due to osmotic pressure is not properly evaluated by this method. As an easy and alternative method to evaluate the water absorption capacity of SAP, Jensen[6] has proposed a new method that used a graduated cylinder. The method consists in measuring the volume change of a certain mass of loosely packed SAP as it absorbs water.

This study focuses on water release from SAP due to osmotic pressure in highly alkaline solution. To evaluate it, two measurement techniques of the tea bag method and the graduated cylinder method were used. Effects of aqueous solutions with different concentrations of ions on the absorption and desorption behavior of different SAPs were investigated. Furthermore, rheological behavior of fresh cement

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pastes with SAP was discussed in relation to the kinetics of the liquid uptake and release of SAP.

2. MATERALS AND EXPERIMENTAL METHODS

2.1 Materials and mixture proportion

Ordinary Portland cement with a Blaine fineness value of $3310 cm^2/g$ was used. A polycarboxylic acid type superplasticizer was used. Two types of SAP (A and B) were used. SAP-A is produced by aqueous polymerization while SAP-B is obtained by inverse suspension polymerization. As shown in Fig.1, SAP-A is irregular shape and contains greater particles. SAP-B is almost mono-sized spherical powders. Tiny particles of SAP-B are gathered around big particles due to a surfactant. Their nominal absorption capacities in alkaline solution are 10.0g/g and 13.3g/g of dry mass, respectively. SAP-B was sieved to obtain two particle size distributions, large (300~600μm) and small (150~300μm). Those properties of SAPs are summarized with notation in Table 1. Water to cement ratio of cement paste was 0.28. Dosage of SAP was determined to absorb 10% of mixing water. Therefore, the water absorbed by SAP to cement ratio was 0.028, so that the effective water to cement ratio of the bulk cement matrix was smaller than 0.28. Mixture proportion of cement pastes is given in Table 2.

2.2 Experimental procedures

(1) The tea bag method

Water absorption capacity of SAP was evaluated by a tea bag method in accordance with JIS K 7223. The absorption capacity of SAP was calculated by the following equation:

$$W = \frac{M_3 - M_2 - M_1}{M_1} \qquad (1)$$

Where $W(g/g)$ is water absorption capacity of SAP, $M_1(g)$ is the mass of SAP under dry condition , $M_2(g)$ is the mass of the te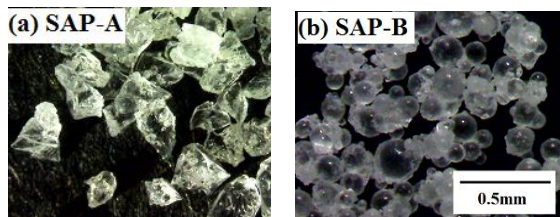a bag which had been pre-wetted in the testing solution, $M_3(g)$ is the mass of the tea bag with the SAP which is hung in a beaker filled with the testing solution for a prescribed time.

(2) The graduated cylinder method

Based on Jensen's proposal[6], the graduated cylinder method is used to simply estimate the water absorption capacity of SAP. The measuring principle and the measured quantities are indicated in Fig.2. The method aims at measuring the volume change of a certain mass of loosely packed SAP when it absorbs water. Primarily, the water absorption capacity at equilibrium is measured. For a SAP with slow water absorption it is necessary to measure at the prescribed time interval. Tests will be carried out in the laboratory at a temperature of 20±2℃ and relative humidity of 60±5%, which is as the same as the tea bag method. The absorption capacity of SAP was calculated by the following equation[6]:

$$K = \frac{\rho_{water}}{\rho_{SAP}} \left[\frac{V_2}{V_1} \cdot \frac{m_1}{m_2} - 1 \right] \qquad (2)$$

Where $K(g/g)$ is water absorption capacity of SAP, $m_1(g)$ is the mass of dry SAP sample which was filling a graduated cylinder to its maximum reading (Fig.2 (a)), $V_1(ml)$ is the volume of dry SAP sample which was filling a graduated cylinder to its maximum reading (Fig.2 (a)), $m_2(g)$ is the mass of the certain, small amount of dry SAP sample which was filled into a graduated cylinder (Fig.2 (b)), $V_2(ml)$ is the volume of swollen SAP sample after settling in the testing solution (Fig.2 (c)), ρ_{water} is the density of water, ρ_{SAP} is the dry, solid density of SAP (Table 1).

(3) Solutions to be absorbed in the absorption capacity tests

Cement past pore solution contains various ionic species, mainly K^+, Na^+, Ca^{2+}, OH^- and SO_4^{2-}. These ions have gradually dissolved from cement particles into pore solution. Good understanding of the time-dependent concentrations of ions in cement paste pore solution is provided by previous research[7]. Concentration of ions changes with time gradually at early ages. At first, concentration of calcium Ca^{2+} remains saturation due to the continuous release from cement compounds and solid portlandite ($Ca(OH)_2$).
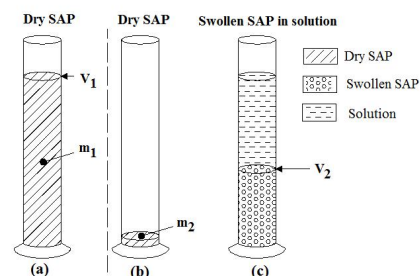

Fig.1 SAP particles at dry state

Table 1 Properties of SAP

SAP	Absorption capacity (g/g)	Particle size (μm)	Density (g/cm³)
SAP-AL	10.0	300~600	1.45
SAP-BL SAP-BS	13.3	300~600 150~300	1.25

Fig.2 Determination of water absorption capacity of SAP by the graduated cylinder method

Table 2 Mixture proportion of cement pastes (mass fraction)

Mixes	W/C	W/Cₑ	C	W	W_SAP	SP	SAP	Initial setting	Final setting
REF	0.28	0.28	1	0.28	-	0.0056	-	3:20	4:51
SAP-AL(10%W)	0.28	0.252	1	0.252	0.028	0.0075	0.0028	3:38	5:56
SAP-BL(10%W)	0.28	0.252	1	0.252	0.028	0.0070	0.0022	3:42	4:46
SAP-BS(10%W)	0.28	0.252	1	0.252	0.028	0.0080	0.0022	3:19	5:34

Then it decreases slowly from about 3hours. Dissolution of alkali sulfates (K_2SO_4 and Na_2SO_4) into pore solution result in an increase in concentrations of K^+ and Na^+. Taking account of those changes, concentration of cations in the solution to be absorbed in the absorption capacity tests was determined. In addition, solutions ①, ②, ③ and ④ were added at the prescribed time interval to simulate pore solution. The sequence of pouring those solutions for the absorption capacity tests is given in Fig.3. The molar concentrations of cations in simulated pore solution are indicated in Table.3.

(4) Rheology test

　　Plastic viscosity of cement pastes was measured with a commercial rheometer (Fig.4). The fresh cement pastes were tested with every 10 minutes after the water addition. After 1 hour, the fresh cement pastes were tested every 30 minutes until losing proper workability. Before each measurement, the cement paste was agitated (i.e.pre-sheared) using a metal bar in order to reduce the effect of possible sedimentation.

　　The measurement is based on the continuous shear rate controlled test. Changes in shear stress τ are a function of shear rate $\dot{\gamma}$ and subsequent derivation of plastic viscosity values according to the Bingham model. To obtain the Bingham parameters, the descending branch of the shear stress-shear strain rate curve was approximated by using linear regression analysis. The intersection of the linear regression line with the slope of the line provided the value of the plastic viscosity μ (Fig.5).

(5) Setting

　　The time of initial and final set was measured on all cement pastes by the Vicart apparatus in accordance with JIS R 5201.

3. RESULTS AND DISCUSSION

3.1 Swelling behavior of SAP evaluated by the tea bag method

　　Fig.6 shows changes in absorption capacity of SAPs with time of immersion in the saturated solution

Fig.4 Schematic drawing of testing apparatus for the rheology test

of calcium hydroxide. After they were dipped for 10 minutes, all the SAPs exhibited their maximum absorption capacities. It is consistent with the common understanding that the absorption of pore solution in the SAP is rapid and takes place in several minutes after mixing[8]. However, when SAP-AL was immersed into the solution for a longer time, its absorption capacity decreased quickly, whereas the absorption capacity of SAP-B decreased gradually. The rate of reduction was not so great that most of absorption capacity was maintained in SAP-B.

　　Fig.7 also shows changes in absorption capacity of SAPs with time. In this test, to evaluate desorption properties at different alkaline conditions, all the SAPs were forced to absorb pure water in advance. Thus, the absorption capacity at the initial period of 30 minutes was much greater than the nominal value, which was given from the manufacturer (Table 1). Further, the maximum absorption capacity of any SAP sample was quite greater than that in saturated calcium hydroxide solution at the initial period of 30 minutes. It is found that greater the outside concentration of the solution, the lower the absorption capacity of the SAP, due to osmotic pressure as the main driving force for the water absorption capacity and resultant swelling. In addition, comparing Fig.7 (a)-(c), the addition of Na^+ showed a obviously stronger desorption of the solution than the addition of Ca^{2+}. Ca^{2+} ions have been found to have a particular strong effect on the absorbency and swelling kinetics of SAP particles. The presence of Ca^{2+} in aqueous solution will dramatically decrease the absorption capacity and alter the absorption and release kinetics of SAP particles[9]. However, as for the SAP used in this study, it seems that impact of the presence of Na^+ cannot be ignored.

Table 3 The molar concentration of cations in simulated pore solution

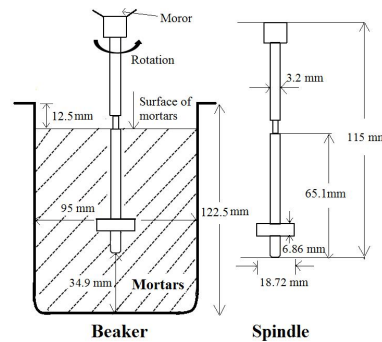| Ion	Ion concentration ($\times 10^{-3}$ mol/L)			
	Solution ①	Solution ②	Solution ③	Solution ④
K^+	41	43	46	50
Na^+	10	10	9.9	11
Ca^{2+}	1.6	1.4	1.4	0.7

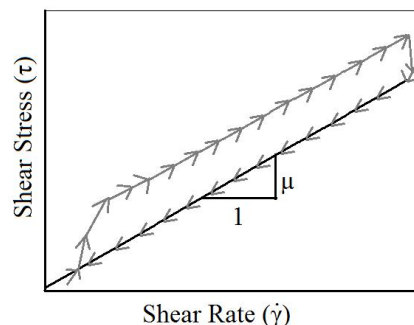Fig.3 Order of using the alkaline solutions for the absorption capacity tests

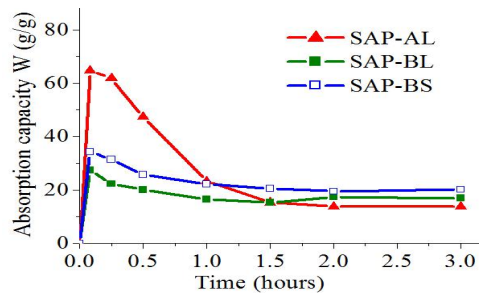

Fig.5 Schematic curve to determine plastic viscosity[5]

Fig.6 Change in absorption capacity in saturated solution of calcium hydroxide by the tea bag method

3.2 Swelling behavior of SAP evaluated by the graduated cylinder method

Fig.8 shows changes in absorption capacity of SAPs with time. SAP-AL exhibited maximum absorption capacity at the value of 600g/g within 30 minutes, almost the double of the value obtained by the tea bag method. The maximum absorption capacities of SAP-B obtained by the graduated cylinder were close to the values obtained by the tea bag. This phenomenon could be related to the shapes of SAPs and the difference in drainage mechanism between two measurement techniques. The shape of SAP-AL is irregular, while SAP-B is spherical shape. In the tea bag method, SAP is drained from excess liquid by means of gravity, which makes particles arrangement closer and increase packing density. In contract to this, in the graduated cylinder method, swollen SAP is buoyant in water and may pack less dense. The absorbed liquid causes SAP-AL to grow as in irregular shape. This increases the spaces between SAP particles and reduces packing density of SAP-AL particles. However, when SAP-B was used, the spaces between spherical particles and packing density have not greatly changed. Thus, the difference in absorption capacity is not so great
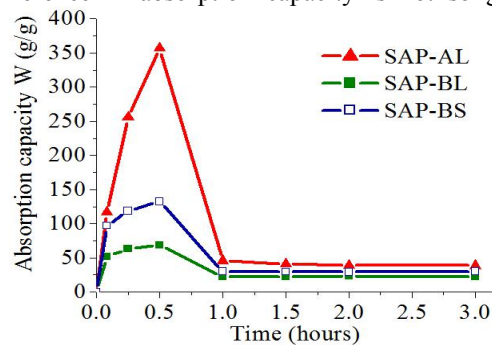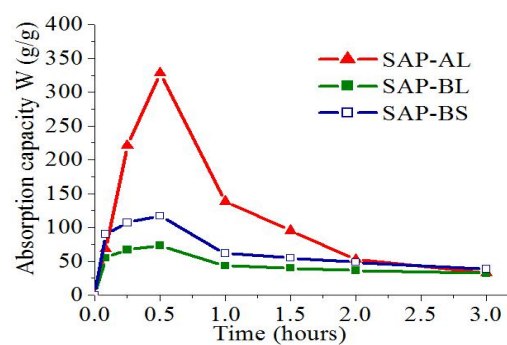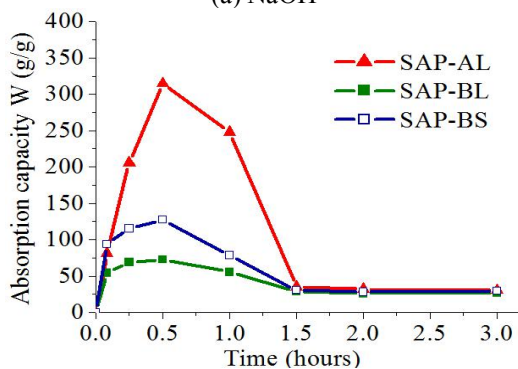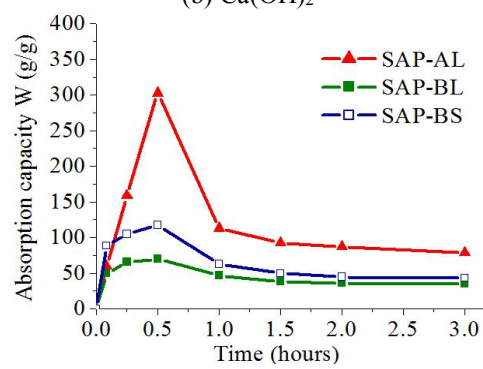
between the two measurement techniques.

When the alkali solutions and the simulated pore solution were added, the absorption capacity of SAP-AL always increased quickly, and then decreased rapidly. Eventually, equilibrium of absorption capacity was reached about immersion for 1 hour. While SAP-B showed a relatively stable and small value of absorption capacity than SAP-AL. In the tea bag method, the similar phenomenon was also observed (Fig.6-7). Furthermore, when SAP-B was used, the smaller SAPs, the relatively greater value of absorption capacity was observed. Luis[10] has reported that small particles of SAP have less absorption capacity since the surfaces of them are less active. The SAP he used is also produced by inverse suspension polymerization as well as SAP-B. Thus, experimental results in this study do not agree with them. In addition, when Ca^{2+} was added into solutions (Fig.8 (b) and (c)), SAP-AL almost released all of the water. This phenomenon may give evidence that the presence of Ca^{2+} in the alkaline solution greatly modified the kinetics of the water release of SAP[9].

In view of all the results obtained by two measuring techniques, SAP-AL produced by aqueous polymerization with irregular shape always showed greater absorption capacity than SAP-B obtained by inverse suspension polymerization with spherical shape. This result is not consistent with the properties provided by the manufacturer (Table 1). Thus, the absorption property of SAP must be interpreted carefully if detailed information on the measurement is not provided. The sizes of particles were also principal elements with respect to the absorption kinetics[10]. Thus, a purposeful choice of SAP should be made as an additive for concrete.

On the other hand, similar variation tendency of absorption capacities of SAP in cementitious systems

(a) NaOH

(b) Ca(OH)₂

(c) Ca(OH)₂+NaOH

(d) Simulated pore solution

Fig.7 Change in absorption capacity with time evaluated by the tea bag method

(a) NaOH

(b) Ca(OH)$_2$
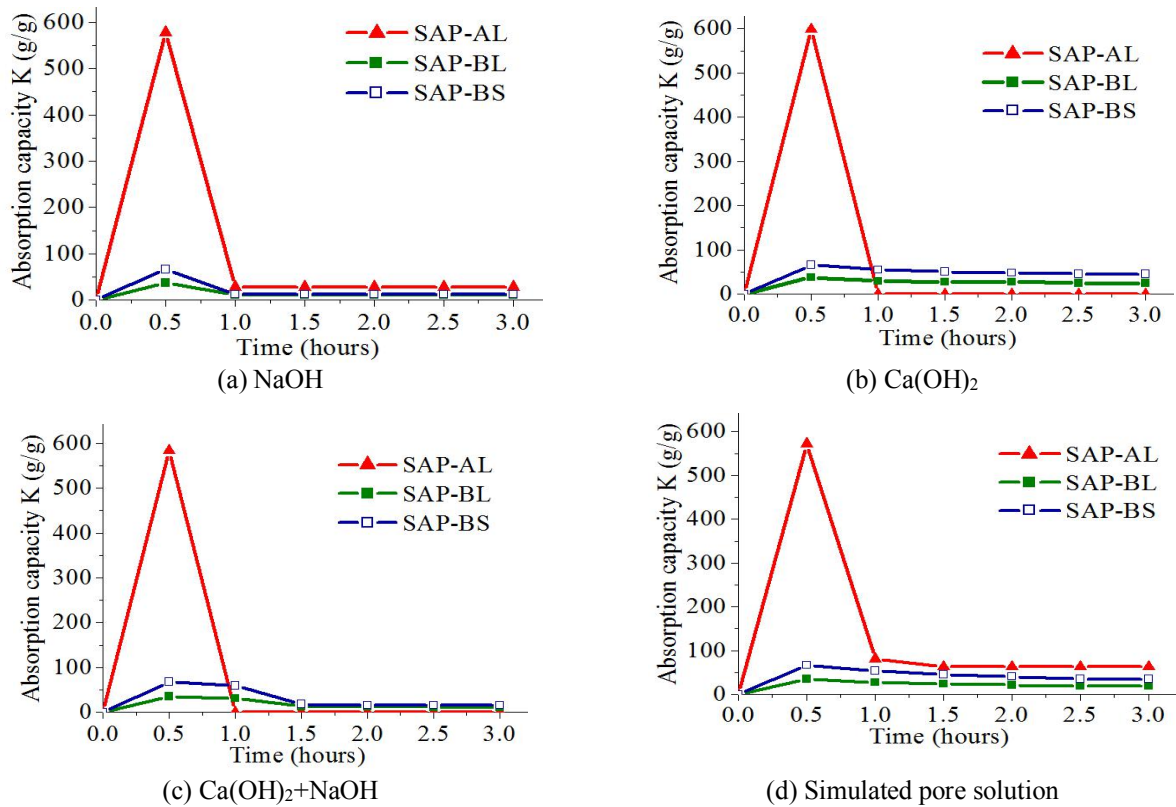
(c) Ca(OH)$_2$+NaOH

(d) Simulated pore solution

Fig.8 Change in absorption capacity with time evaluated by the graduated cylinder method

could be obtained either by the tea bag method with a complex series of steps, or by the graduated cylinder method with simple steps. However, when SAPs are used for the purpose of water control on rheology modification, various situations in terms of alkaline environment are expected in practical application. Further investigation is necessary to establish a proper measurement technique to evaluate swelling and absorption capacity of SAP in cement environment. However, at least the graduated cylinder method gives the consistent results with those of the tea bag method. Furthermore, effects of osmotic pressure may be considered in the testing conditions. Therefore, the graduated cylinder method can be used as a simple way to evaluate absorption and desorption capacity of SAP under more similar conditions to real concrete.

3.3 Effect of SAP addition on plastic viscosity of cement paste

Fig. 9 shows time-dependent changes in plastic viscosity of the cement pasts. The reference specimens and ones with SAP-BL exhibited rapid increases in
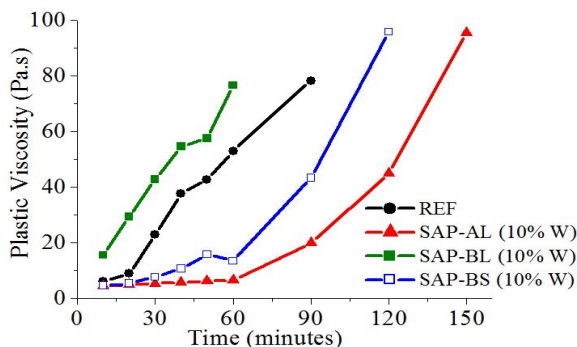

Fig.9 Development of plastic viscosity at early age

plastic viscosity right from the beginning of the measurements. Cement pastes with SAP-AL and BS kept a stable value of plastic viscosity at first, and then started increasing rapidly about from 60 minutes. In other words, when SAP-AL and BS were used, the time at which plastic viscosity started increasing was delayed. In particular, the cement pastes with SAP-AL showed the slowest growth in plastic viscosity. These behaviors could be related to the hydration process of cement even at very early ages before setting. Sun et al.[11] have investigated the development of viscosity in cement pastes with different water to cement ratios. They also observed the early increase in viscosity before the initial setting. They attributed the early viscosity development to the dormant period in cement hydration. As shown in Table 2, the mixtures with SAP-AL and BS showed the longer final setting while almost the same initial setting was observed among the cement pastes. This fact suggests that the evolution of microstructure during the dormant period is different among the specimens with different SAPs. The early release of water from SAP may affect the internal friction or breaking the agglomerated structure of cement particles. Furthermore, it should be noted that the decrease in effective water to cement ratio from 0.28 to 0.252 did not lead the early setting of cement pastes. This also suggests that the water released from SAP affects subsequent progress of hydration of cement.

The development of the plastic viscosity in Fig. 9 also corresponds to the sorption kinetics observed in the tea bag method and the graduated cylinder method. Increase in plastic viscosity may result from the decrease in freely available water in cementitious

system and may mean the increase in internal friction of material. These changes in the plastic viscosity were recorded before the initial setting time when the water of SAP had released already. The water released from SAP would supply the freely available water as a lubricant to alleviate internal friction and postpone the growth of plastic viscosity. Here, all the specimens with SAP in this study have the same amount of 10% of mixing water with SAP. Relatively large scale desorption of water from SAP-AL at early age would prevent the quantity of freely available water from diminishing quickly, leading to the slowest growth in plastic viscosity. On the contrary, SAP-BL showed relatively stable and the least value of absorption capacity than SAP-AL and SAP-BS (Fig. 7 and 8). When SAP-BL absorbed 10% of mixing water, the freely available water in cement paste with SAP-BL was less than that in the reference specimens, thus at the first point of time measured, the value of plastic viscosity of cement paste with SAP-BL was higher than that of the reference. Later, the freely available water was not supplemented effectively from SAP-BL. This caused rapid increase in plastic viscosity of cement paste with SAP-BL.

On the other hand, although SAP-BS absorbed almost the same amount of water as SAP-BL during mixing process, the value of plastic viscosity were almost close to the reference at the first point of time measured. It may be related to the density of SAP particles and the moisture distributions in cementitious system. Since the particle sizes of SAP were different, the numbers of SAP particles were different among the cement pastes. Therefore, their spatial distribution, in other words, the number densities of internal water reservoirs were different among the specimens at the beginning. In addition when the internal water was released, the initial distributions of moisture were also different among the specimens. This could affect the initial evolution of internal friction.

4. CONCLUSIONS

The kinetics of the liquid uptake and release of SAPs were investigated. Major results obtained in this study are as follows：

(1) The greater concentration of the solution, the lower the absorption capacity of the SAP. SAPs produced by aqueous polymerization showed greater absorption capacity than SAPs obtained by inverse suspension polymerization. The greater the kinetics of the liquid uptake, the rapider the kinetics of the liquid release.

(2) The similar variation tendency of absorption capacities of SAP could be obtained by two measurement techniques. The graduate cylinder method is considered as a useful way to evaluate absorption capacity in cement environment.

(3) The development of plastic viscosity could be related to the water released from SAP. It affects subsequent progress of hydration even in the dormant period.

(4) The addition of SAP affects the development of

the plastic viscosity, since it change the amount of freely available water to alleviate internal friction. The particle sizes of SAP and the differences initial distributions of moisture could affect the initial evolution of internal friction.

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