

博 士 学 位 論 文

Ph.D. Dissertation

Absorption and desorption behaviors of
superabsorbent polymers and their effects on
volume changes in cement-based materials

金沢大学大学院自然科学研究科
Graduate School of Natural Science and Technology
Kanazawa University

環境デザイン学専攻

学籍番号: 1424052007

氏 名: 胡 巧英

主任指導教員名: 五十嵐 心一

提出年月: 2017年9月25日

Contents

Contents

Chapter 1 Introduction.....	1
1.1 Background and scope.....	1
1.1.1 Early age cracking of high-performance concrete.....	1
1.1.2 Autogenous shrinkage.....	2
1.1.3 Autogenous Expansion.....	6
1.1.4 Internal curing.....	8
1.2 Objective.....	10
REFERENCES.....	12
Chapter 2 Properties of superabsorbent polymers.....	16
2.1 Introduction.....	16
2.2 Absorption behavior of SAP.....	17
2.3 Desorption behavior of SAP.....	20
2.4 Conclusions.....	23
REFERENCES.....	24
Chapter 3 Materials and experimental procedures.....	27
3.1 Materials.....	27
3.2 Experimental.....	29
3.2.1 Evaluation of water absorption capacity of SAP.....	29
3.2.2 Immersion solutions for water absorption capacity measurement of SAP.....	32
3.2.3 Evaluation for mortars and cement pastes with SAP.....	33
REFERENCES.....	40
Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials.....	41
4.1 Introduction.....	41
4.2 Kinetics of water absorption and desorption of SAP measured by the tea bag method and the graduated cylinder method.....	42
4.2.1 Swelling behavior of SAP evaluated by the tea bag method.....	42
4.2.2 Swelling behavior of SAP evaluated by the graduated cylinder method.....	44
4.3 Comparison of absorption capacity of SAP measured by the modified tea bag method and the filtration method.....	46
4.3.1 Swelling behavior of SAP evaluated by the modified tea bag method.....	46
4.3.2 Swelling behavior of SAP evaluated by the filtration method.....	48
4.3.3 Comparison of absorption capacity measured by the two methods.....	49

Contents

4.4 Effect of SAP on plastic viscosity of cement pastes at early age.....	51
4.4.1 Mixture proportion.....	51
4.4.2 Results and discussion.....	51
4.5 Effect of SAP on plastic viscosity of mortars at early age.....	53
4.5.1 Mixture proportion.....	53
4.5.2 Results and discussion.....	53
4.6 Conclusions.....	54
REFERENCES.....	56
Chapter 5 Early age autogenous deformation of mortars with low water to cement ratio.....	58
5.1 Introduction.....	58
5.2 Influence of bleed water on early age volume changes in mortars with low water to cement ratios.....	59
5.2.1 Mixture proportion.....	59
5.2.2 Results and discussion.....	60
5.3 Effects of SAP on expansive behavior of mortars at early ages.....	65
5.3.1 Mixture proportion.....	65
5.3.2 Results and discussion.....	66
5.4 Conclusions.....	70
REFERENCES.....	72
Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials.....	74
6.1 Introduction.....	74
6.2 Effect of partial gelation of mixing water with SAP on autogenous shrinkage behavior of cement paste with low water to cement ratio.....	75
6.2.1 Mixture proportion.....	75
6.2.2 Results and discussion.....	76
6.3 Effect of gelation of mixing water with SAP on early age properties of mortars with high water to cement ratios.....	82
6.3.1 Mixture proportion.....	82
6.3.2 Results and discussion.....	83
6.4 Conclusions.....	89
REFERENCES.....	90
Chapter 7 Conclusions.....	92
Acknowledgments.....	95

Chapter 1 Introduction

1.1 Background and scope

1.1.1 Early age cracking of high-performance concrete

With the aid of superplasticizers and additives such as silica fume [1, 2], high-performance concrete (HPC) is generally characterized by high strength and early age strength, low permeability and diffusion, high durability and long life in corrosive environments [3, 4]. These remarkable properties of HPC are mostly achieved by properly proportioning the mixtures on a low water to cement ratio [5]. However, coming with other drawbacks, early age cracking potential of concrete is higher than that in ordinary concrete with conventional water to cement ratio [6, 7]. Depending on several factors including free shrinkage and thermal deformation, early age cracking is a complex phenomenon which causes serious problems with regard to workability and durability of HPC [8].

Cracking of HPC is expected to occur when volume changes associated with shrinkage are restrained internally or externally, and development of tensile stress exceeds the materials strength [9]. Kovler and Zhutovsky [10] have divided the reasons of non-structural cracking of concrete into two parts: chemical reactions and moisture changes. Likewise, the driving forces for shrinkage were divided into two classes by Weiss [11]: thermal-related shrinkage and moisture shrinkage. The former includes the early age volume changes which are induced by the heat generated during hydration, such as hydration shrinkage and thermal shrinkage. The later includes the early age volume changes which are induced by internal and external moisture conditions. In general, thermal related shrinkage and moisture shrinkage are frequently interrelated and occur concurrently. This study focuses on autogenous shrinkage, which occurs primarily as a result of chemical shrinkage due to the hydration reaction and self-desiccation due to internal water consumption by the hydration reaction [12]. On the other hands, to assess the cracking associated with shrinkage, it is critical to view all aspects of shrinkage in different stages. Holt [13] has divided shrinkage of concrete into two stages: early ages and later ages. The early age refers to the concrete within 24 hours. Later ages, or long-term age is defined as the age of 24 hours and beyond. Early age cracking associated with shrinkage occurs immediately after casting, since that concrete has the lowest tensile strain capacity and most internal stresses sensitivity [13].

1.1.2 Autogenous shrinkage

(1) Terminology

Autogenous shrinkage was first decried by Lynam in 1934 [14]: Cement paste will obey the general law of gel formation and contract its volume. It is convenient to refer to this type of shrinkage as “autogenous shrinkage” to distinguish it from others which are due to thermal causes or loss of moisture to the air. The following terminology was proposed by the Japan Concrete Institute committee [12]:

1) Autogenous shrinkage is defined as the macroscopic volume reduction of cementitious materials when cement hydrates after initial setting. Likewise, autogenous expansion is defined as the macroscopic volume increase of cementitious materials when cement hydrates after initial setting. Autogenous shrinkage and expansion do not include volume change due to loss or ingress of substances, temperature variation, application of an external force and restraint. Autogenous deformation, or autogenous volume change includes autogenous shrinkage and autogenous expansion [12, 14-15]. In this thesis, autogenous shrinkage is plotted as negative and autogenous expansion as positive.

2) Chemical shrinkage is absolute volume reduction associated with the hydration reactions in a cementitious material. Autogenous shrinkage is a result of chemical shrinkage. Schematic representation of early age volume change of a sealed cement paste is given in Fig.1-1. Chemical shrinkage is considered to be internal volume reduction, while autogenous shrinkage is considered to be the reduction of the external volume due to solid skeleton formation.

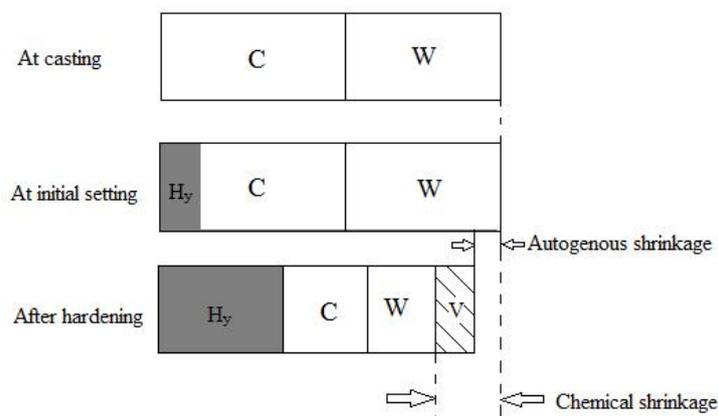


Fig.1-1 Schematic representation of early age volume change of a sealed cement paste [12]

(C: unhydrated cement, W: unhydrated water, Hy: hydration products, V: voids generated by hydration)

3) Self-desiccation is a phenomenon that hardens in cement paste, which is subject to drying due to the consumption of capillary water in the progress of cement hydration. It is also caused by chemical shrinkage.

(2) Mechanisms of autogenous shrinkage

The actual mechanisms of autogenous shrinkage are not well understood. However there is general agreement about the relationship between autogenous shrinkage and chemical shrinkage, and the relationship between autogenous shrinkage and self-desiccation. According to Fig.1-1, autogenous shrinkage can be divided into three stages: before setting, hardening transition with setting and hardened stage [16].

Chemical shrinkage before setting may be completely converted into a bulk deformation of the cementitious system [14]. Hammer [16] has simultaneously conducted volumetric tests of chemical shrinkage and autogenous shrinkage (Fig.1-2). In the early age before setting when the cement paste is still fluid, autogenous shrinkage is equivalent to chemical shrinkage. Hydration of cement grains begins immediately on contact with water. In the early period with a low degree of hydration, the pre-induction period lasts only a few minutes for initial reaction of C_3A with gypsum and water to form ettringite (Fig.1-3). Then a protective layer is formed around cement grains in the dormant period for several hours. Therefore, in this stage, chemical shrinkage results from the external volume reduction due to the reactions of hydration.

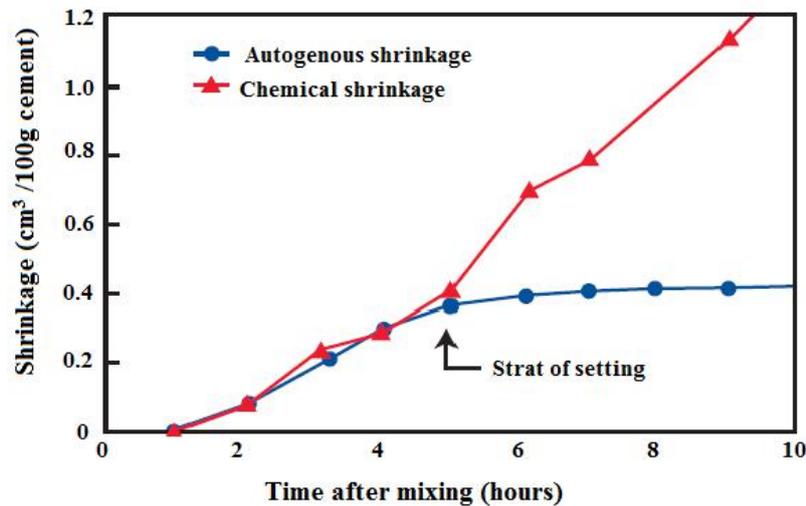


Fig.1-2 Relationship between autogenous shrinkage and chemical shrinkage of cement past with water to binder ratio of 0.40 and 5% of silica fume [17]

Chapter 1 Introduction

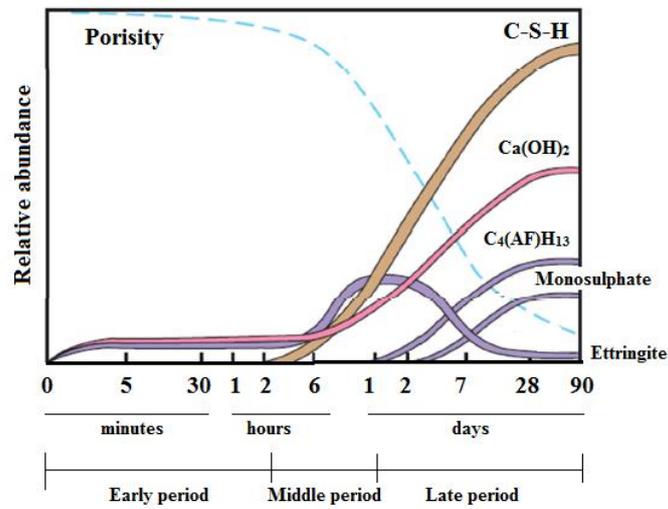


Fig.1-3 Three periods of cement hydration and relative volume contents of major products [18]

From the middle period of hydration, the external chemical shrinkage is ended at the suspension-solid transition when all cement grains are in contact with water and the hydrates percolate in cementitious systems [19]. When the first solid paths are formed with the increase in stiffness, the cementitious systems can resist some of the volume change stresses in the hardening paste. Autogenous shrinkage is changing from being a function of chemical shrinkage versus self-desiccation. In other words, following the suspension-solid transition and self-restriction, autogenous shrinkage becomes dominant in early age cement systems (Fig.1-3). Soon after the initial skeleton is formed, a change in the pore structure of the cementitious system takes place. With progress of hydration process, empty pores start to nucleate and grow in the bigger pores [20]. The water-air menisci form (Fig.1-4), and the increase in curvature of menisci continues is pulled into the capillary pores and causes hydrostatic tensile stresses on the capillary pores walls, which lead to the bulk deformation of the cement paste, called autogenous

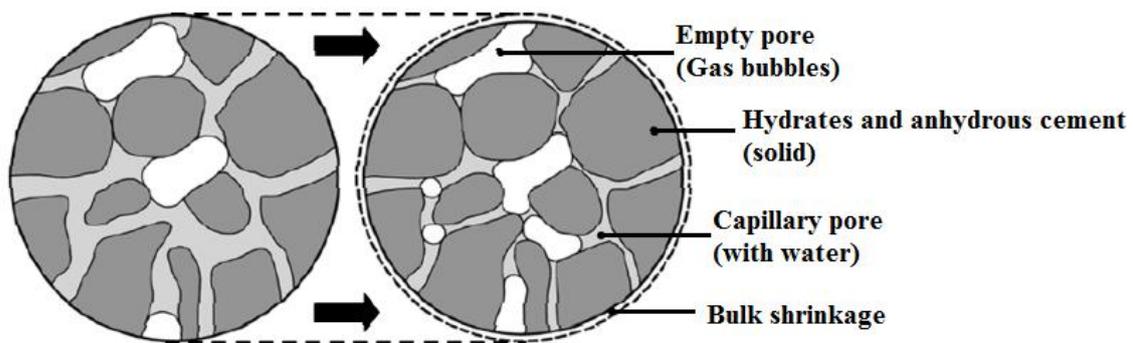


Fig.1-4 Schematic representation of a cross-section of hydrating cement paste [21,22] (Left: low degree of hydration. Right: high degree of hydration)

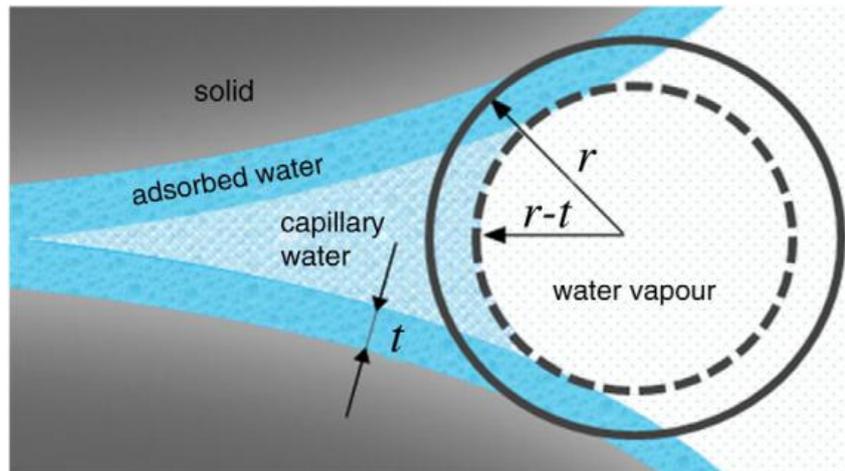


Fig.1-5 Schematic representation of menisci and adsorbed water layer in capillary pore [23]

shrinkage [21-23].

In the hardened stage, autogenous shrinkage occurs due to self-desiccation when a rigid skeleton is formed to resist volume changes. When the localized water is consumed in the paste for the hydration, the relative humidity decreases [24]. As the water is drawn out of the capillary pore, the thickness of the adsorbed water layer on the surface of the pore walls changes (Fig.1-5), resulting in changes both in the surface tension of the solids and in the disjoining pressure of absorbed water between solid surfaces [22, 23]. Thus accompanied by continuous decrease of the internal RH, the capillary pores are progressively emptied by chemical shrinkage, referred to as self-desiccation [21, 22]. The mechanism can be summed up as proposed in Fig.1-6.

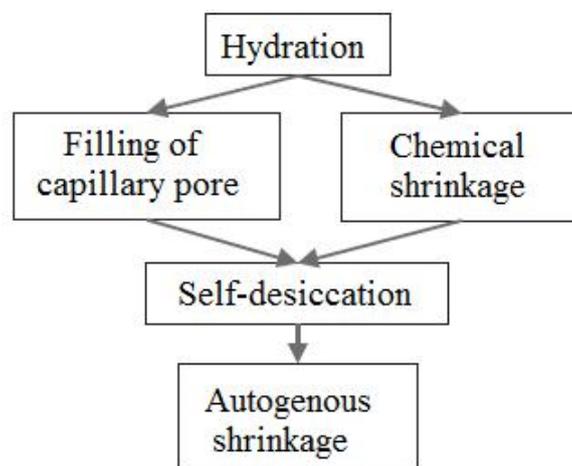


Fig.1-6 Mechanism of autogenous shrinkage [19]

1.1.3 Autogenous Expansion

When cement paste with high water to cement ratio is cured contentiously in water from the time of placing, an outer expansion will be observed, since the pore system of cement paste is supposed to remain saturated throughout hydration [25]. The swelling is considerably small, approximately 100×10^{-6} to 150×10^{-6} , when reached 6 to 12 months after casting for a mix with cement content 300 kg/m^3 . However, although it is cured under water, cement pastes with low water to cement or large dimensions decrease their length, since curing water only permeates into external of specimen while internal part is subjected to self-desiccation [26]. In that case, length change of the specimen results from the internal autogenous shrinkage exceeding the expansion. If autogenous shrinkage is a balance between self-desiccation and initial expansion, the resulting deformation can be measured [19]. Considering initial expansion, the mechanism of autogenous shrinkage at an early age can be summed up in Fig.1-7, which is modified from Fig.1-6.

Mechanism of the expansion is not fully understood. Three primarily reasons have been proposed for the expansion [3-5]: (1) thermal dilation, (2) deposition of hydration products and (3) uptake of bleed water after setting time. The increase of temperature due to the exothermic nature of the hydration reactions will cause development of thermal gradients within concrete mass. This effect occurs simultaneously with autogenous shrinkage at early age [27]. The mechanisms of total thermal deformation in partially-saturated concrete are divided into three parts: (1) pure thermal dilation of constituents, (2) thermal shrinkage and swelling (due to redistribution of water from gel to capillary pores and resulting shrinkage with increasing temperature) and (3) RH changes due to the temperature changes [28]. The coefficient of

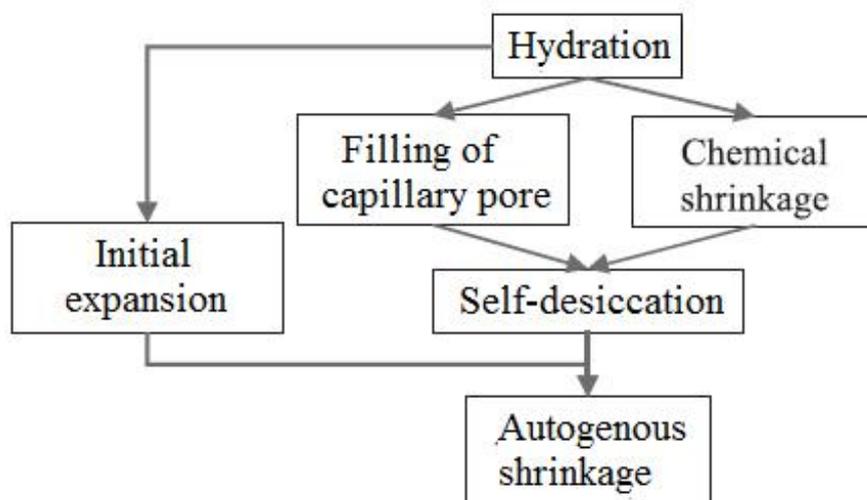


Fig.1-7 Proposed mechanism of autogenous shrinkage at early age [19]

Chapter 1 Introduction

thermal expansion (CTE) of cement-based materials is often assumed a constant default value in calculation of thermal dilation. However, it strongly depends upon concrete mix constituents, particular aggregate type, and time [29]. The CTE due to pure thermal dilation has been shown to be practically independent of the moisture content of the medium of mix constituents [27]. The increase in RH, which due to the increase of temperature in a partially-saturated porous, results in the increase in the overall CTE [30].

The formation of hydration products could be responsible for expansion. The hydration products form a spatial network in the cement-based system, even when the reaction products have a lower volume than the reactants [14]. Internal pressure, which is generated due to the growth of further hydration products inside the spatial network, may cause moderate swelling of the system [31]. Ettringite formation may be responsible for expansion. Metha [32] have concluded that expansion associated with ettringite formation was mainly due to water absorption. The wet cured specimen swells so much, whereas the dry cured specimen does not show significant expansion. However, the study by Odler and Colán-Subauste [33] supported that the expansion were related to oriented growth of ettringite. The uptake of water from the environment was not essential for the expansion associated with ettringite. Deng and Tang [34] have suggested that expansive forces result from crystallization pressure as well as swelling pressure converted from the reduction of chemical potentials in the reaction of ettringite formation. They also have concluded that the hydroxyl concentration of the pore solutions played an important role by regulating the distribution and morphology of ettringite crystals in the cement paste [35]. However, it is different to make any clear conclusion about the mechanism of expansion by the formation of hydration products, especially the formation of ettringite crystals.

The bleed water reabsorption has been suggested to be the main source of expansion at early age due to alteration of the moisture state of the cement-based system. Bjøntegaard et al. [36] have removed the bleed water from the samples, or added extra water to the existing bleed. The subsequent effects of removing or adding water on the water to cement ratio of the mix may contribute the differences in the observed expansion of and autogenous deformation. When the cement paste was rotated during hardening, negligible early age expansion due to bleed water reabsorption was observed by Mohr and Hood [37]. Thus they suggested that bleed water reabsorption was the primary mechanism causing initial expansion in sealed autogenous deformation specimen. The influence of early transient expansion due to bleed water reabsorption is obviously associated with mixture design of the cement-based materials. Mixture with very low water to cement ratio, bleed water is largely eliminated [8].

1.1.4 Internal curing

(1) Terminology

RILEM committee ICC-Internal Curing of Concrete [38] have classified internal curing into two parts:

- 1) Internal water curing (sometimes called “water entertainment”), when the curing agent performs as a water reservoir, which gradually releases water.
- 2) Internal sealing, when the curing agent is intended to delay or prevent loss of water from the hardening concrete.

For high-performance concrete (HPC) with low water to cement ratio, internal curing is preferable since internal sealing is unable to prevent self-desiccation.

In 2010, the American Concrete Institute (ACI) defined internal curing as “supplying water throughout a freshly placed cementitious mixture using reservoirs, via pre-wetted lightweight aggregates, that readily release water as needed for hydration or to replace moisture lost through evaporation or self-desiccation.” Two major objectives of internal curing, maximizing hydration and minimizing self-desiccation, are identified by this definition. The difference between external and internal curing is shown in Fig.1-8 [39]. The internal agent is distributed uniformly and spaced close enough to provide coverage for the entire paste system. It can overcome the problem of low permeability of a low water to cement ratio system, which is not solved by traditional external curing.

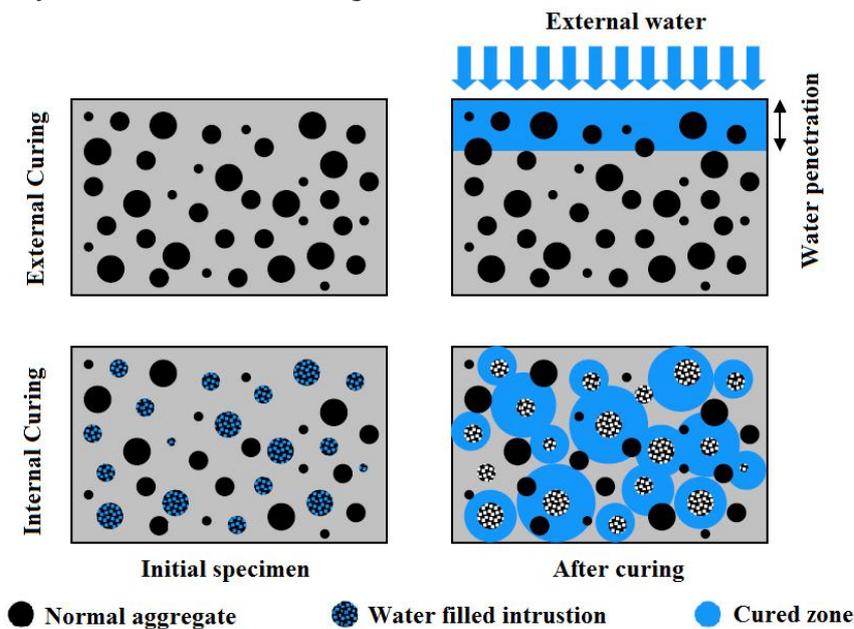


Fig.1-8 Illustration of the difference between external and internal curing [40]

(2) Internal water curing using lightweight aggregate

Weber and Reinhardt [40] introduced a new type of high performance concrete by replacing 25% by volume of the aggregates by prewetted lightweight aggregate (LWA). The partial replacement of aggregate with prewetted LWA creates water storage inside the concrete, which supports continuous wet curing. This method was named as autogenous curing. The results showed that this method was effective for increasing the degree of hydration of cement in a low water to cement ratio concrete [40]. Bentur et al. [41] investigated restrained autogenous shrinkage in high-strength lightweight aggregate concrete by the same method. The experiments showed that high-strength concrete without autogenous shrinkage could be obtained by this method. They suggested that this method was very effective in eliminating the autogenous shrinkage, due to the internal supply of water from the saturated LWA. Golias et al. [42] have suggested that the mass of LWA for internal curing was directly related to the LWA's degree of saturation. The degree of saturation of the LWA increases, the volume of LWA required to supply the required volume of internal curing water decreases [42]. Bentz and Snyder [43] considered the availability and spatial proximity of the additional water introduced via the saturated lightweight fine aggregate instead of the coarse lightweight aggregate, since the much higher surface area will result in a more uniform distribution of the additional curing water. They suggested a well dispersed system of the water reservoirs would be most beneficial to the internal curing process. Since a shorter transport distance of internal water from the aggregate surface increases the potential degree of hydration, so that the internal curing process is increased.

(3) Internal water curing using superabsorbent polymer

Jensen and Hansen [44] used superabsorbent polymer (SAP) as internal water entertainment to mitigate self-desiccation in HPC. During mixing of the concrete, SAP absorbs water and forms hydrogel containing free water. Water entrained in the SAP is consumed during cement hydration to provide internal curing to the surrounding paste matrix. With a rate of 0.6% by weight of cement, corresponding to an entrained water to cement ratio of 0.07, SAP was added into cement paste with water to cement ration of 0.3. The self-desiccation of the cement paste was totally avoided. Meanwhile, an expansion of about 800 microstrains was measured in the first day of hardening. From 2 days to 3 weeks after water addition, the expansion decreased to approximately 50 microstrains [45]. Using SAP as water entertainment has similarities to LWA addition, but SAP can be used as a dry concrete admixture. Furthermore, the undesirable addition of a large amount of mechanically poor aggregate particles is avoided [44].

Chapter 1 Introduction

Nowadays, apart from the usage as internal curing additives for reducing autogenous shrinkage, new application of SAP to concrete has been of great interest. As additives for water control, the incorporation of SAP is effective in modifying the rheology [46]. Snoeck et al. [47] investigated the ability of SAP to promote self-sealing and self-healing in cementitious materials by the combination of microfibers and SAP under two different realistic conditions. Lee et al. [48] measured the flow of sodium chloride solution through cracked cement paste and mortars with SAP to assess the effect of SAP on self-sealing. Mechtcherine et al. [49] have focused on the freeze-thaw resistance of ordinary concrete modified by the addition of SAP. Therefore, a more detailed study is required to investigate the properties of SAP and its effect on cement-based materials. The introduction of SAP will be discussed later.

1.2 Objective

This study deals with autogenous deformation of HPC and internal curing with SAP as a means to reduce early age autogenous shrinkage. This study is divided into 7 chapters, its schematic outline is shown in Fig.1-9. The main part of this study consists of three parts, corresponding to studies on kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials (Chapter 4), early age autogenous deformation of mortars (Chapter 5) and effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials (Chapter 6). The abstracts of the three chapters are as follows:

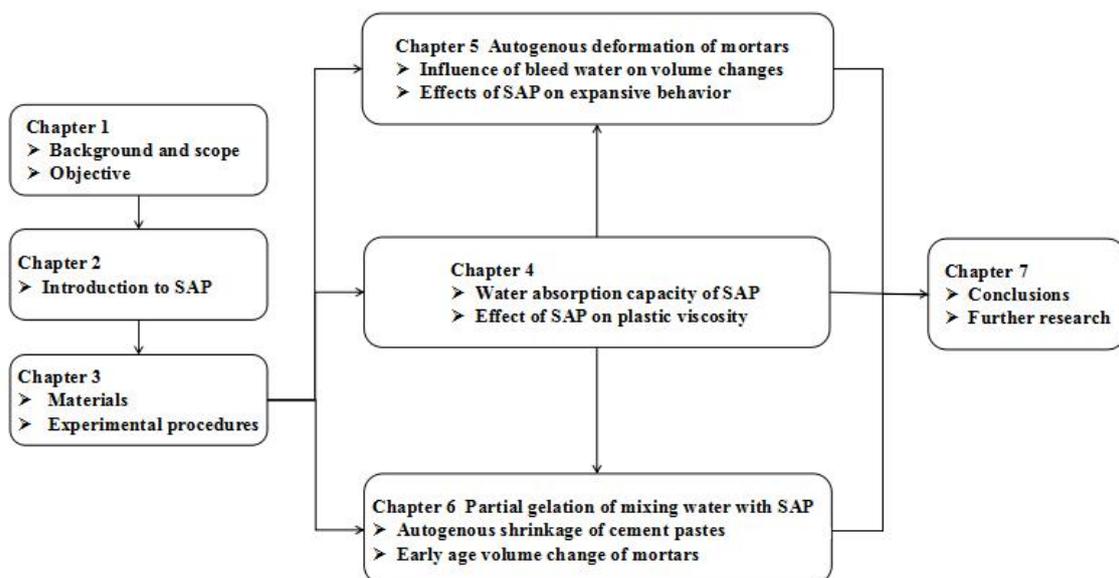


Fig.1-9 Outline of this study

Chapter 1 Introduction

Chapter 4: This chapter focuses on comparison of absorption capacity of SAP measured by the tea bag method, graduated cylinder method and the filtration method using de-ionized water, simulated pore solution and cement slurry filtrate. Effects of aqueous solutions with different concentrations of ions on the absorption and desorption behavior of different SAPs are investigated. The comparison between the results of absorption capacities is discussed from the viewpoint of retention of interparticle liquid on SAP particles during the test period. Furthermore, rheological behavior of fresh cement pastes and mortars with SAP is discussed in relation to the kinetics and sorption capacity of SAP. In this study, autogenous deformation of cement-based materials are investigated with an emphasis on absorption and desorption behaviors of SAP. Therefore, this chapter is the basis of Chapter 5 and Chapter 6.

Chapter 5: The objective of this chapter is to investigate the effects of bleed water and SAP addition on the autogenous deformation behaviors at very early ages. Reabsorption of bleed water of mortars with superplasticizer and viscosity enhancement agent addition are discussed in relation to the initial expansion. Then, the evolution of microstructure in mortars with SAP is also discussed in relation to the expansion at early ages.

Chapter 6: In this chapter, cement pastes and mortars with SAP are produced with additional water and without additional water. This chapter focuses on effect of gelation of a part of mixing water with SAP on early age properties of the cementitious materials. Comparisons between the results of autogenous shrinkage, workability and mechanical properties at early age are discussed from the viewpoint of hydrogel formation due to SAP in different water contents.

Chapter 1 Introduction

REFERENCES

- [1] Aïtcin, P. C.,” High performance concrete,” E & FN Spon, London, pp. 162-214, 1998.
- [2] Malier, Y.,” Introduction in high-performance concrete: From material to structure,” E & FN Spon, London, pp. 14-33, 1992.
- [3] Kosmatka, S. H. et al.,” Design and Control of Concrete Mixture,” Portland Cement Association, pp. 229-314, 2003.
- [4] Aïtcin, P. C.,” The durability characteristics of high performance concrete: a review,” Cement and Concrete Composites, Vol. 25, No. 4-5, pp. 409-420, 2003.
- [5] Mehta, P.K. and Monteiro, P. J. M.,” Concrete Microstructure, Properties, and Materials,” McGraw-Hill Education, pp. 479-491, 2005.
- [6] Bentur, A.,” Early age shrinkage and cracking in cementitious systems,” Proceedings of the international RILEM symposium on shrinkage, pp. 1-20, 2000.
- [7] Mounanga, P. et al.,” Early-age autogenous cracking of cementitious matrices: Physico-chemical analysis and micro/macro investigations,” Materials and Structures, Vol. 44, No. 4, pp. 749-772, 2011.
- [8] Bentur, A.,” Early age cracking in cementitious systems,” Tunnelling and Underground Spave Technology, Vol. 59, pp. 215-220, 2016.
- [9] Briffaut, M., Benboudjema, F. and D’Aloia, L.,” Effect of fibers on early age cracking of concrete tunnel lining. Part I: Laboratory ring test,” RILEM TC 181-EAS Committee, pp. 1-12, 2002.
- [10] Kovler, K. and Zhutovsky, S.,” Overview and future trends of shrinkage research,” Materials and Structures, Vol. 39, pp. 827-847, 2006.
- [11] Weiss, J.,” Prediction of early age shrinkage cracking in concrete elements,” PH.D. Thesis, Northwestern University, pp. 8-30, 1999.
- [12] Tazawa, E.,” Japan Concrete Institute. Technical committee report on autogenous shrinkage of concrete: Proceedings of International Workshop on Autogenous shrinkage of concrete,” E & FN Spon, London, pp. 3-26, 1999.
- [13] Holt, E. and Leivo, H.,” Cracking risks associated with early age shrinkage,” Cement and Concrete Composites, Vol. 26, No. 5, pp. 521-530, 2004.
- [14] Lura, P.,” Autogenous deformation and internal curing of concrete,” p.H.D. Thesis, Delft University Press, pp. 3-34, 2003.
- [15] Bentz, D. P. and Jensen, O. M.,” Mitigation strategies for autogenous shrinkage cracking,” Cement and Concrete Composites, Vol. 26, No. 6, pp. 677-685, 2004.
- [16] Hammer, T. A.,” Test methods for liner measurement of autogenous shrinkage before setting,” Autogenous Shrinkage of Concrete, edited by Ei-ichi Tazawa, E & FN Spon,

Chapter 1 Introduction

- London, pp. 143-154, 1999.
- [17] Holt, E.,” Early age autogenous shrinkage of concrete,” Technical Research Centre of Finland, VTT Publications, Espoo, pp. 32-47, 2001.
- [18] Peter, Hewlett.,” Lea’s chemistry of cement and concrete,” Elsevier, Great Britain, p. 11053, 1998.
- [19] Barcelo, L., Moranville, M. and Clavaud, B.,” Autogenous shrinkage of concrete: a balance between autogenous swelling and self-desiccation,” Cement and Concrete Research, Vol. 35, No. 1, pp. 177-183, 2005.
- [20] Lura, P. et al.,” Early-age acoustic emission measurements in hydrating cement paste: Evidence for cavitation during solidification due to self-desiccation,” Cement and Concrete Research, Vol. 39, No. 10, pp. 861-867, 2009.
- [21] Jensen, O.M. and Hansen, P. F.,” Autogenous deformation and RH-change in perspective,” Cement and Concrete Research, Vol. 31, No. 12, pp. 1859-1865, 2001.
- [22] Lura, P., Jensen, O.M. and Breugel, K.,” Autogenous shrinkage in high-performance cement paste: An evaluation of basic mechanisms,” Cement and Concrete Research, Vol. 33, No. 2, pp. 223-232, 2003.
- [23] Chen, H. et al.,” Prediction of self-desiccation in low water-to-cement ratio pastes based on pore structure evolution,” Cement and Concrete Research, Vol. 49, pp. 38-47, 2013.
- [24] Koenders, E. A. B. and Breugel, K.,” Numerical modelling of self-desiccation of hardening cement paste,” HERON, Vol. 43, No. 2, pp. 99-118, 1998.
- [25] Neville, A. M.,” Properties of Concrete,” Person Education Limited, pp. 395-397, 2011.
- [26] Tazawa, E. and Miyazawa, S.,” Experimental study of mechanism of autogenous shrinkage of concrete,” Cement and Concrete Research, Vol. 25, No. 8, pp. 1633-1638, 1995.
- [27] Sellevold, E. J. And Bjøntegaard, Ø.,” Coefficient of thermal expansion of cement paste and concrete: Mechanisms of moisture interaction,” Materials and Structure, Vol. 39, No. 9, pp. 809-815, 2006.
- [28] Wyrzykowski, M. and Lura, P.,” Controlling the coefficient of thermal expansion of cementitious materials-A new application for superabsorbent polymers,” Cement and Concrete Composites, Vol. 35, No. 1, pp. 49-58, 2013.
- [29] Uygunoglu, T. and Topçu, B.,” Thermal expansion of self-consolidating normal and lightweight aggregate concrete at elevated temperature,” Construction and Building Materials, Vol. 23, No. 9, pp. 3063-3069, 2009.
- [30] Wyrzykowski, M. and Lura, P.,” Moisture dependence of thermal expansion in cement-based materials at early age,” Cement and Concrete Research, Vol. 53, pp. 25-35, 2013.

Chapter 1 Introduction

- [31] Bažant, Z. P. and Wittmann, F. H.,” Creep and Shrinkage in Concrete Structures,” John Wiley & Sons, p. 363, 1982.
- [32] Mehta, P. K.,” Mechanism of expansion associated with ettringite formation,” Cement and Concrete Research, Vol. 3, No. 1, pp. 1-6, 1973.
- [33] Odler, I. and Colán-Subauste, J.,” Investigations on cement expansion associated with ettringite formation,” Cement and Concrete Research, Vol. 99, No. 5, pp. 731-735, 1999.
- [34] Deng, M. and Tang, M.,” Formation and expansion of ettringite crystals,” Cement and Concrete Research, Vol. 24, pp. 119-126, 1994.
- [35] Chen, W.,” Hydration of slag cement: Theory, Molding and Application,” PH.D. Thesis, University of Twente, p. 170, 2006.
- [36] Bjøntegaard, Ø., Hammer, T. A. and Sellevold, E. T.,” On the measurement of free deformation of early age cement past and concrete,” Cement and Concrete Composites, Vol. 26, No. 5, pp. 427-435, 2004.
- [37] Mohr, B.J. and Hood, K.L.” Influence of bleed water reabsorption on cement paste autogenous deformation,” Cement and Concrete Composites, Vol. 40, No. 2, pp. 220-225, 2010.
- [38] RILEM: Internal Curing of Concrete, State-of-the-art Report of RILEM Technical Committee 196-ICC, Edited by Kovler, K. and Jensen, O, RILEM Publications S. A. R. L, pp. 7-8, 2007.
- [39] Bentz, D. and Weiss, J.” Internal Curing: A 2010 State-of-the-Art Review,” NIST Interagency/Internal Report (NISTIR)-7765, pp. 1-3, 2011.
- [40] Weber, S. and Reihardt, H. W.,” A New Generation of High Performance Concrete: Concrete with Autogenous Curing,” Advanced Cement Based Materials, Vol. 6, No. 2, pp. 59-68, 1997.
- [41] Bentur, A. Igarashi, S. and Kovler, K.,” Prevention of autogenous shrinkage in high-strength concrete by internal curing using wet lightweight aggregates,” Cement and Concrete Research, Vol. 31, No. 11, pp. 1587-1597, 2001.
- [42] Golias, M. Castro, J. and Weiss, J.,” The influence of the initial moisture content of lightweight aggregate on internal curing,” Construction and Building Materials, Vol. 35, pp. 52-62, 2012.
- [43] Bentz, D. P. and Snyder, K. A.,” Protected paste volume in concrete: Extension to internal curing using saturated lightweight fine aggregate,” Cement and Concrete Research, Vol. 29, No. 11, pp. 1863-1867, 1999.
- [44] Jensen, O.M. and Hansen, P.F.,” Water-entrained cement-based materials I. Principles and theoretical background,” Cement and Concrete Research, Vol. 31, No. 4, pp. 647-654, 2001.

Chapter 1 Introduction

- [45] Jensen, O.M. and Hansen, P.F.,” Water-entrained cement-based materials: II. Experimental observations,” *Cement and Concrete Research*, Vol. 32, No. 6, pp. 973-978, 2002.
- [46] Mechtcherine, V., Egor, S. and Christof, S.” Effect of superabsorbent polymers (SAPs) on rheological properties of fresh cement-based mortars-Development of yield stress and plastic viscosity over time,” *Cement and Concrete Research*, Vol. 67, pp.52-65, 2015.
- [47] Snoeck, D. et al.,” Self-healing cementitious materials by the combination of microfibers and superabsorbent polymers,” *Journal of Intelligent Material Systems and Structures*, Vol. 25, No. 1, pp. 13-24, 2014.
- [48] Lee, H. X. D., Wong, H. S. and Buenfeld, N.,” Self-sealing cement-baste materials using superabsorbent polymers,” *Proc. International RILEM Conference on Use of Superabsorbent Polymer and other new Additives in Concrete*, (Jensen, O.M., Hasholt, M.T. and Laustsen, S. eds.) RILEM S. A. R. L, Lyngby, Denmark, pp.171-178, 2010.
- [49] Mechtcherine, V. et al.,” Effect of superabsorbent polymers (SAP) on the freeze-thaw resistance of concrete: results of a RILEM interlaboratory study,” *Materials and Structure*, Vol. 50, No. 14, pp. 1-19, 2017.

Chapter 2 Properties of superabsorbent polymers

2.1 Introduction

Superabsorbent polymer (SAP) is a group of cross-linked polyelectrolyte which start to expand contact with aqueous fluids resulting in the formation of a hydrogel [1]. SAP has the ability to absorb a significant amount water from the surrounding and to retain water within their structure without dissolving [2]. The swelling process of SAP is shown in Fig.2-1 [1]. The polymer backbone in SAP is hydrophilic due to water loving carboxylic acid groups ($-\text{COOH}$). Because of the excellent ability of absorption as mention above, SAP has been frequently used, especially in healthy industry.

Since Jensen and Hansen [2, 3] proved that SAP significantly reduced autogenous shrinkage, SAP has evolved as a promising and multifunctional additive in construction industries. As internal curing materials, the internal curing efficiencies of SAP and partially saturated LWA were compared by Geiker et al. [4]. They found that for mortars containing the same quantity of internal water, SAP had a beneficial efficient in reducing autogenous shrinkage at late ages compared to the LAW, due to a more uniform distribution of the internal water reservoirs. The maintenance of a substantially higher internal RH was also observed with

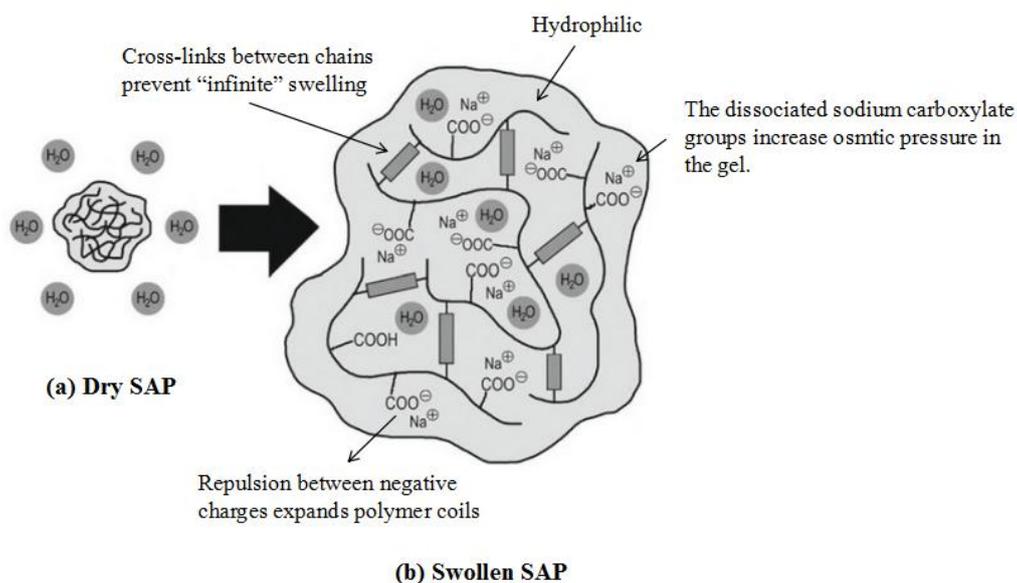


Fig.2-1 The swelling process of SAP [1]

(SAP based on poly acrylic acid is used, in which electrical neutrality is maintained because sodium ions are trapped in the hydrogel)

Chapter 2 Properties of of superabsorbent polymers

internal curing. As additives with respect to water control, application of SAP to concrete has been of great interest. Incorporation of SAP is effective in modifying the rheological properties of concrete or mortars in fresh state. Mechtcherine et al. [5] have investigated the combined effects of SAP and extra water on the development of rheological properties in fresh mortars. They found that the major factor that governed the rheological properties of fresh mortar was the distinct kinetics of water uptake inherent in the SAP samples, as governed by their particular chemical structures. Snoeck et al. [6] investigated the relationship between water penetration and self-sealing of cracks in cementitious materials with SAP. The results showed that when SAP was added into specimens, water permeability through a crack and capillary absorption in a crack were reduced. The swollen SAP sealed the crack and recovered the water-tightness of the structure. Lee et al. [7] measured the flow of sodium chloride solution through cracked cement paste and mortars with SAP to assess the effect of SAP on self-sealing. A reduced cumulative flow was observed in specimens with SAP. The results also suggested that the larger SAP particles were more effective for sealing cracks.

From the above, the application of SAP in construction is all about water. It is essential to understand absorption and desorption mechanism. In this section, theoretical background about absorption and desorption mechanism are will discussed together with results in the literature.

2.2 Absorption behavior of SAP

SAP can increase their volume immediately as soon as they contact with water, reaching saturation with a few minutes (Fig.2-2 (a)-(b)). The main mechanism of absorption behavior of SAP is osmotic pressure which is dependent on the ionic nature of the aqueous fluids. The osmotic pressure inside a dry SAP is relatively high due to gathering of the ions in SAPs. The chemical potential gradient of osmotic pressure within SAP polymer network compared to the external environment makes SAPs begin to absorb aqueous fluid [10]. By absorption of aqueous fluid, the charge in the polymer network is diluted and the osmotic pressure is reduced inside the SAP (Fig.2-1). The forces of the polymer network, mainly of neutralization of the polyacrylate and cross-link, and external osmotic pressure are working together to weaken the osmotic drying force. SAP becomes saturated when all the forces are in balance. Therefore, the ion concentrations of aqueous fluid can significantly affect the absorption capacity of SAP [8]. Fig.2-3 shows effect of the ion concentration on the absorption capacity of SAP. A smaller absorption capacity of SAP is observed when SAP was immersed in aqueous fluid with a higher ion concentration. On the other hand, without specifying ion concentrations of aqueous fluid,

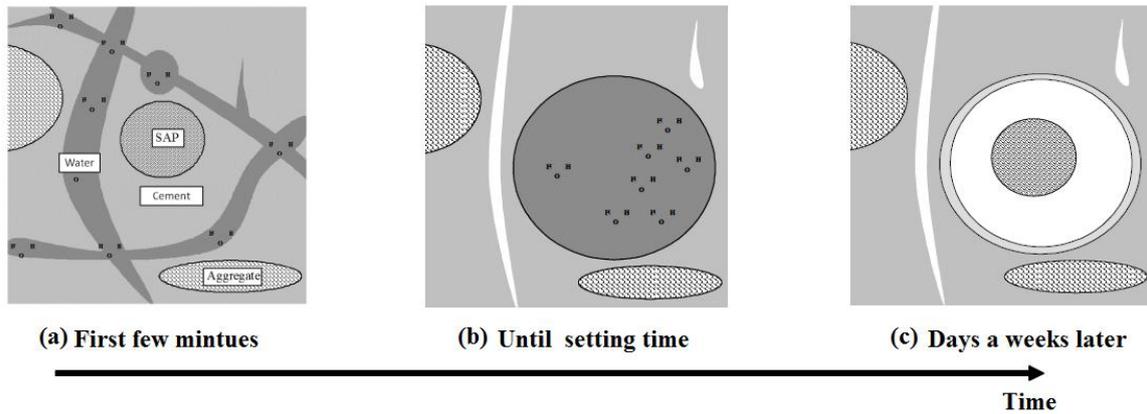


Fig.2-2 Schematic of the change of SAP in cementitious material [9]

(a): Initial condition, homogenous dispersion of cement particle, water, SAP and aggregates; (b): Saturation of SAP; (c): Water desorption of SAP, an almost empty pore remains

SAP could freely swell by absorbing distilled water without putting any load on SAP [11]. When SAP is forced to absorb alkaline saline solution, the absorption capacity of SAP is dramatically reduced. In particular the presence of Ca^{2+} and Al^{3+} ions could remarkably decrease the absorption of SAP. Since the potential ionic cross-link formation with multi-valent ions in the polymer network of SAP hinders swelling [10, 12].

Various types of ions, mainly of K^+ , Na^+ , Ca^{2+} , OH^- and SO_4^{2-} , are dissolved gradually into the pore solution of cement pastes. Previous studies [13-15] have provided a good understanding of the hydration time-dependent concentrations of ions in cement paste pore solution. Recent research works focus on the absorption capacity of SAP in cement paste pore

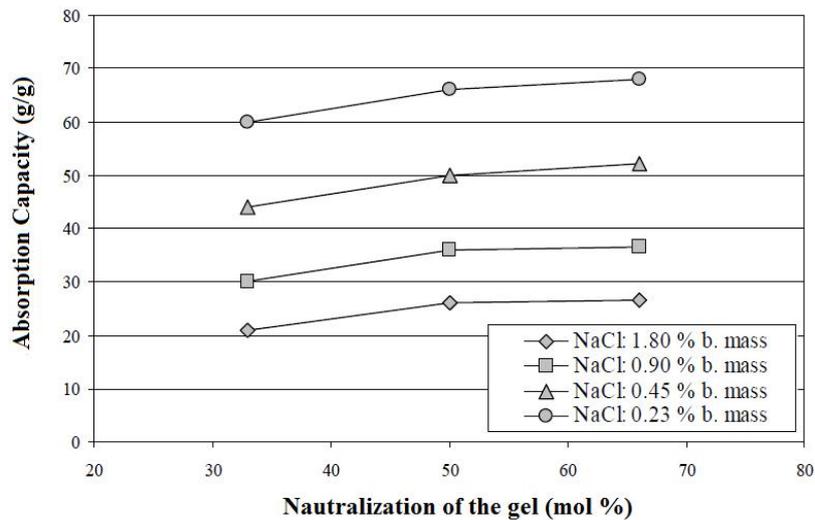


Fig.2-3 Absorption capacity of SAP with different concentrations of NaCl solution [9]

Chapter 2 Properties of of superabsorbent polymers

solution. Synthetic pore fluid was often used to measure the water absorption capacity of SAP with the intended purpose as an admixture in cement-based materials. Jensen and Hansen [3] measured the absorption capacity of SAPs supplied from two different manufactures. The synthetic pore fluid was composed of $[\text{Na}^+] = 400 \text{ mmol/L}$, $[\text{K}^+] = 400 \text{ mmol/L}$, $[\text{Ca}^{2+}] = 1 \text{ mmol/L}$, $[\text{SO}_4^{2-}] = 40 \text{ mmol/L}$, $[\text{OH}^-] = 722 \text{ mmol/L}$. Their results suggested that the particle sizes of the SAP affected the absorption behaviors. The same synthetic pore fluid was also used by other researchers [16]. Esteves [17] examined the physical state of SAP distribution in synthetic pore fluid by means of optical microscopy and subsequent image analysis. The synthetic pore fluid he used was composed of $[\text{Na}^+] = 200 \text{ mmol/L}$, $[\text{K}^+] = 500 \text{ mmol/L}$, $[\text{Ca}^{2+}] = 1 \text{ mmol/L}$, $[\text{SO}_4^{2-}] = 15 \text{ mmol/L}$, $[\text{OH}^-] = 672 \text{ mmol/L}$. His results indicated that the lower the particle size, the faster the absorption process (Fig.2-4). However, practically, it is difficult to correctly determine the ion concentration of synthetic pore fluid at early ages, since it depends on many factors such as types of cements and time. Instead of synthesized pore solution, cement slurry filtrate has been used because of its simple preparation and similarity to the pore solution [18, 19]. The current activity of RILEM TC 260-RSC “Recommendations for Use of Superabsorbent Polymers in Concrete Construction” (Chair: Prof. V. Mechtcherine, TU Dresden) has proposed cement slurry filtrate for assessing a qualitative estimate of the absorption capacity of SAP. Although the situation of synthetic pore fluid and cement slurry filtrate are different from the environment in cement mixture, the two liquids could be used for preliminary test to disclose fundamental properties towards practical application in cement-based construction materials.

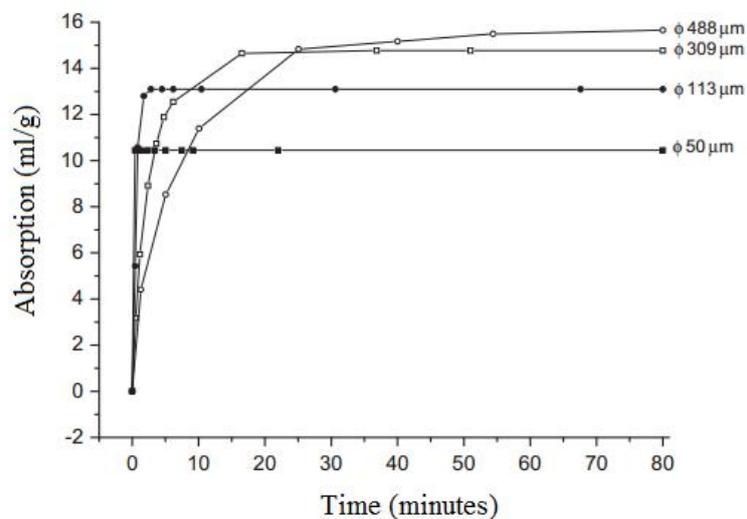


Fig.2-4 Absorption capacity of individual polymer particles with different particle sizes in synthetic pore fluid [17]

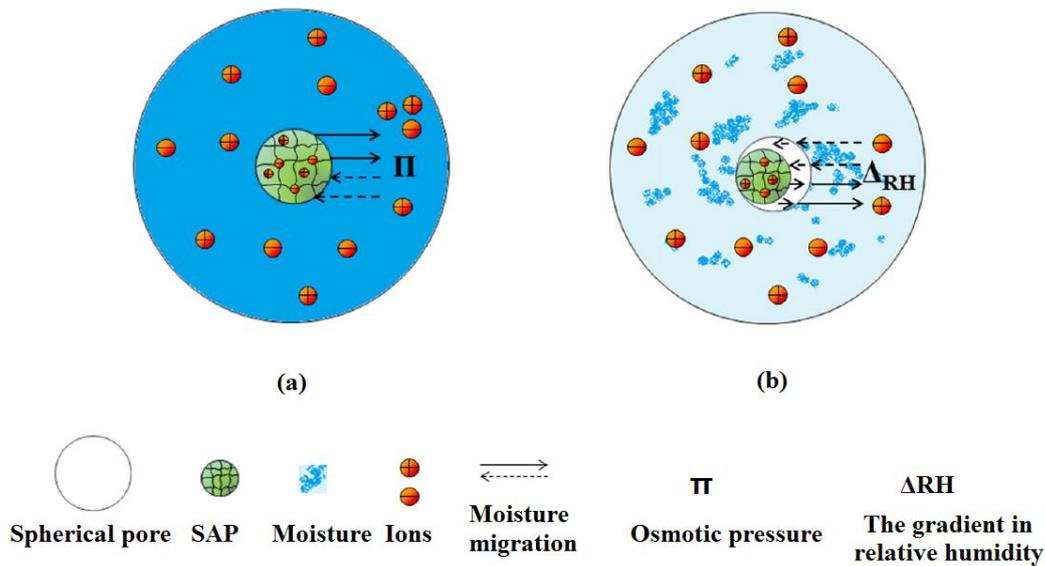


Fig.2-5 Schematic of the desorption of SAP with spherical in the cement paste [21]

2.3 Desorption behavior of SAP

At the late period of hydration, the absorbed water inside SAP is released gradually to the cement matrix, and voids created by SAP are remain (Fig.2-2 (c)). The main driving force for desorption of SAP is the osmotic pressure and the gradient in relative humidity (ΔRH) [20]. As shown in Fig.2-5 (a), at the beginning, the absorbed water is released from SAP due to osmotic pressure which results from the relative lower concentration of ions within the SAP's polymer network compared to the external environment. After the separation of SAP and spherical pore

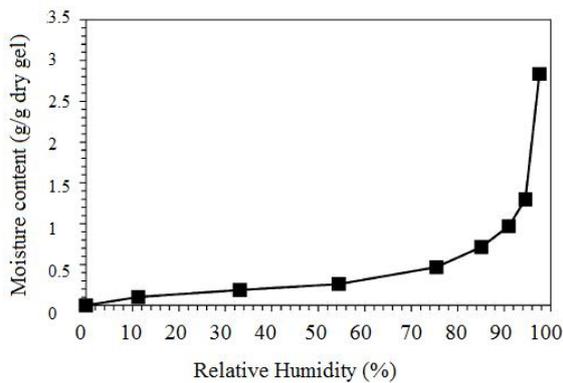


Fig.2-6 Sorption isotherm for SAP [3]
(Absorption capacity: 350 g/g in distilled water; 37 g/g in synthetic pore fluid)

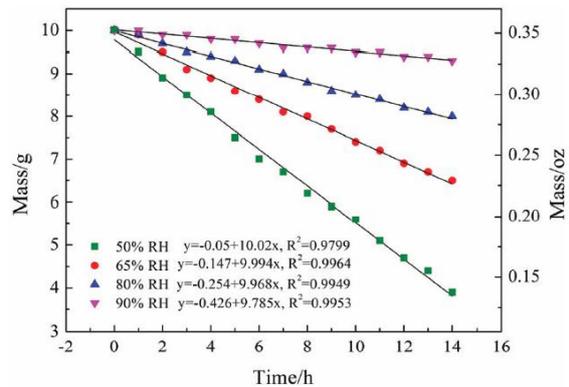


Fig.2-7 Mass-time changes of saturated SAP with different RH [20]
(Absorption capacity: 115 g/g in distilled water; 18 g/g in synthetic pore fluid)

Chapter 2 Properties of of superabsorbent polymers

wall, which is formed by saturated SAP, the relative humidity gradient becomes the main driving force for the further desorption of SAP (Fig.2-5 (b)). The relative humidity gradient is generated between the water in the SAP and the pore fluid when the cement paste do self-desiccate due to hydration [22]. Therefore, as an effective additive for internal curing, desorption of SAP should occur at an appropriate time.

Jensen and Hansen [3] proposed sorption isotherm to indicate the water content in solution-polymerized SAP at reduced RH controlled by saturated salt solutions (Fig.2-6). Wang et al. [20] simulated inverse suspension polymerized SAP with different RH to discuss the water release of SAP in different humidity environments (Fig.2-7). The results of two researchers are consistent. The higher the RH, the more the water release from SAP. In the first days of hydration in HPC with low water to cement ratio, almost all the absorbed water could be released, due to the rapid self-desiccation [1]. Trtik et al. [23] used neutron tomography to observe water released from saturated SAP (Particle size: a diameter of about 1 mm in the dry state and 2.5 mm in the swollen state) in a harden cement paste with water to cement ratio of

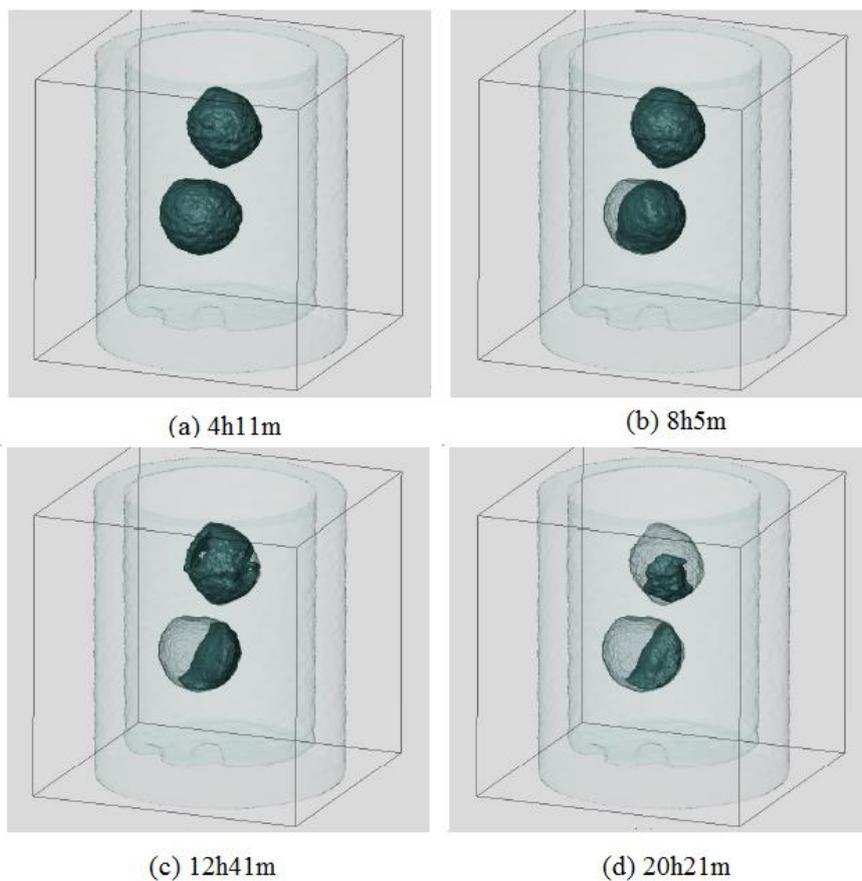


Fig.2-8 3D representation changes of SAP particles in cement paste [23]

(The two darker regions are SAP particles, the upper one was added into the cement paste at dry state; the bottom one was added into the cement paste at saturated state)

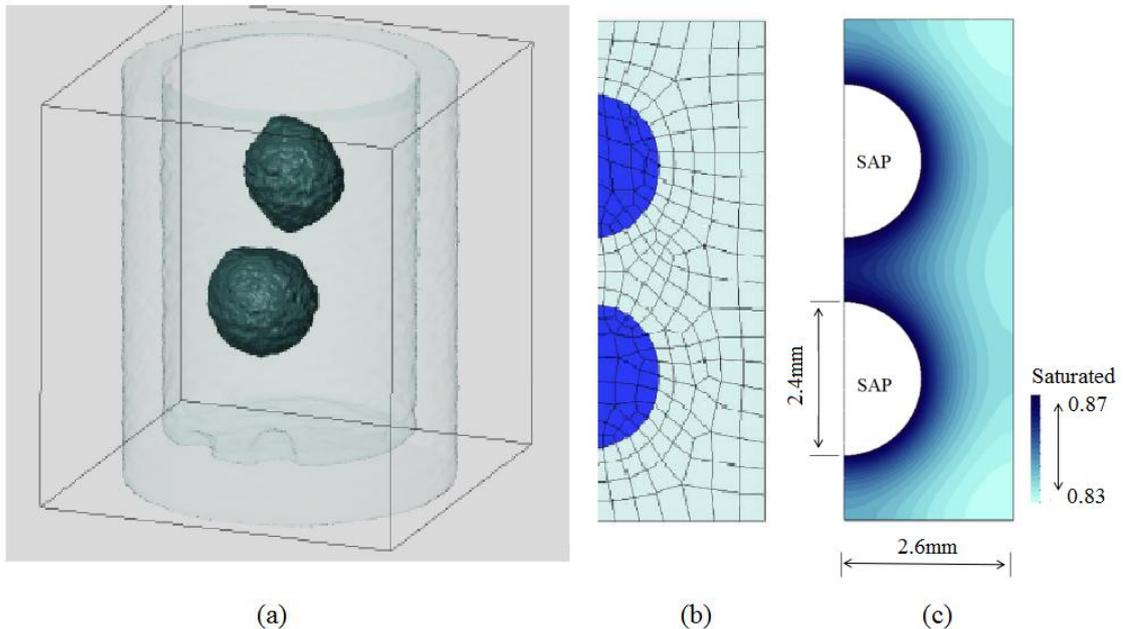


Fig.2-9 Molding of water migration in cement paste [25]

- (a) Tomography image of the specimen by Trtik et al. [23];
- (b) The axisymmetric analysis in the cement paste with SAP;
- (c) Saturation degree distribution in the cement paste with SAP at the age of 150h after the initial setting, when the maximum gradient of saturation degree was observed. The saturation degree of SAP was about 6% at that time.

0.25 (Fig.2-8). The saturated SAP started to release water at around the setting time, and most of the entrained water was released from SAP in the first day of hydration. Nestle et al. [24] used time domain NMR relaxometry for non-destructive studies of the water balance between different sizes of SAP particles and a cement matrix. Their results indicated that SAP absorbed water fast and release of the water from SAP occurred around the setting time. The results also indicated the water release almost finished after 1 day in case of the small particle SAP and after 2 days in the large particle SAP. Wyrzykowski et al. [25] applied a mechanistic-type numerical model of cementitious materials for analysis of water migration from SAP into hydrating cement paste with water to cement ratio of 0.25. The numerical analysis was based on the experimental work by Trtik et al. [23] as mentioned above. The results indicated that a maximum migration distance of 2.2-2.5mm was observed from large SAP (Particle size: a diameter of about 2.4 mm in the swollen state) to cement matrix when the effective permeability dropped to an extremely low level (Fig.2-9).

2.4 Conclusions

In this chapter, the current understanding about absorption and desorption behaviors of SAP is briefly reviewed. The osmotic pressure is the main drying force for absorption of SAP. The absorption behavior of SAP in the water and pore solution is well understood. The desorption behavior of SAP results from the osmotic pressure and the gradient in relative humidity. Various experiments have been done to estimate the water released from SAP and water migration from SAP reservoirs to the surrounding cement matrix. However, more information about absorption and desorption behaviors of SAP in actual cementitious environment is needed, since it is quite complex and hardly controlled at present.

REFERENCES

- [1] Mechtcherine, V. and Reinhardt, H. W.,” Application of Superabsorbent polymer (SAP) in Concrete Construction,” State of the Art Report Prepared by the RILEM TC 225-SAP, Springer., Dordrecht, the Netherlands, pp. 14-32, 2012.
- [2] Jensen, O.M. and Hansen, P.F.,” Water-entrained cement-based materials I. Principles and theoretical background,” Cement and Concrete Research, Vol. 31, No. 4, pp. 647-654, 2001.
- [3] Jensen, O.M. and Hansen, P.F.,” Water-entrained cement-based materials: II. Experimental observations,” Cement and Concrete Research, Vol. 32, No. 6, pp. 973-978, 2002.
- [4] Geiker, M. R., Bentz, D.P. and Jensen, O. M.,” Mitigating Autogeneous Shrinkage by Internal Curing,” ACI SP-218, High Performance Structural Lightweight Concrete, Eds. Ries, J. P. and Holm, T. A, pp. 143-154, 2004.
- [5] Mechtcherine, V., Egor, S. and Christof, S.” Effect of superabsorbent polymers (SAPs) on rheological properties of fresh cement-based mortars-Development of yield stress and plastic viscosity over time,” Cement and Concrete Research, Vol. 67, pp.52-65, 2015.
- [6] Snoeck, D. et al.,” Visualization of water penetration in cementitious materials with superabsorbent polymers by means of neutron radiography,” Cement and Concrete Research, Vol. 42, No. 8, pp. 1113-1121, 2012.
- [7] Lee, H. X. D., Wong, H. S. and Buenfeld, N.,” Self-sealing cement-baste materials using superabsorbent polymers,” Proc. International RILEM Conference on Use of Superabsorbent Polymer and other new Additives in Concrete, (Jensen, O.M., Hasholt, M.T. and Laustsen, S. eds.) RILEM S. A. R. L, Lyngby, Denmark, pp.171-178, 2010.
- [8] Mechtcherine, V. et al.,” Effect of superabsorbent polymers (SAP) on the freeze-thaw resistance of concrete: results of a RILEM interlaboratory study,” Materials and Structure, Vol. 50, No. 14, pp. 1-19, 2017.
- [9] Mönnig, S.,” Superabsorbing additions in concrete - applications, modelling and comparison of different internal water sources,” PH.D. Thesis, University of Stuttgart, pp. 54-91, 2009.
- [10] Zhu, Q. et al.,” Effect of ionic crosslinking on the swelling and mechanical response of model superansorbent polymer hydrogels for internally cured concrete,” Materials and Structures, Vol. 48, No. 7, pp.2261-2276, 2015.
- [11] Mohammad, J, Zohuriaan, M. and Kourosch, K,” Superabsorbent Polymer Materials: A Review,” Iranian Polymer Journal, Vol. 17, No. 6, pp.451-477, 2008.
- [12] Schröfl, C., Mechtcherine, V., and Gorges, M.,” Relation between the molecular structure

Chapter 2 Properties of of superabsorbent polymers

- and the efficiency of superabsorbent polymers (SAP) as concrete admixture to mitigate autogenous shrinkage,” *Cement and Concrete Research*, Vol. 42, No. 6, pp. 865-873, 2012.
- [13] Thomas, N. L. and Double, D. D.,” Calcium and silicon concentrations in solution during the early hydration of Portland cement and tricalcium silicate,” *Cement and Concrete Research*, Vol. 11, No. 5-6, pp. 675-687, 1981.
- [14] Lothenbach, B. and Winnefeld, F.,” Thermodynamic modelling of the hydration of Portland cement,” *Cement and Concrete Research*, Vol. 36, No.2, pp. 209-226, 2006.
- [15] Rajabipour, F., Sant, G. and Weill, J.,” Interactions between shrinkage reducing admixtures (SRA) and cement paste’s pore solution,” *Cement and Concrete Research*, Vol.37, No.5, pp. 606-615, 2008.
- [16] Wang, Y. J., Li, M. and Tian, Q.,” Water release process of superabsorbent polymers in cement paste at early age,” *Internal RILEM Conference on Materials, Systems and Sturcture in Civil Engineering: Conference segment on Service Life of Cement-Based Materials and Structures*, RILEM Publications, pp. 241-247, 2016.
- [17] Esteves, L. P.,” Superabsorbent polymers: On their interaction with water and pore fluid,” *Cement and Concrete Composites*, Vol. 33, No. 7, pp. 717-724, 2011.
- [18] Snoeck, D. et al.,” Visualization of water penetration in cementitious materials with superabsorbent polymers by means of neutron radiography,” *Cement and Concrete Research*, Vol. 42, No. 8, pp. 1113-1121, 2012.
- [19] Snoeck, D. et al.,” The effects of superabsorbent polymers on the microstructure of cementitious materials studied by means of sorption experiments,” *Cement and Concrete Researc*, Vol. 77, pp. 26-35, 2015.
- [20] Wang, F. et al.,” Study on mechanism of desorption behavior of saturated superabsorbent polymers in concrete,” *ACI Materials Journal*, No. 112-M44, pp. 463-470, 2015.
- [21] Wang, F. et al.,” Influence of superabsorbent polymers on the surrounding cement paste,” *Cement and Concrete Research*, Vol. 81, No. 8, pp. 112-121, 2016.
- [22] Lura, P., Jensen, O. M. and Igarashi, S.,” Experimental observation of internal water curing of concrete,” *Materials and Structures*, Vol. 48, No. 40, pp.211-220, 2007.
- [23] Trtik, P. et al.,” Neutron tomography measurements of water release from superabsorbent polymers in cement paste,” *Proceeding of the International RILEM Conference on Material Science (MatSci)*, PRO 77, RILEM Publications, pp. 175-185, 2010.
- [24] Nestle, N. et al.,” Water balance and pore structure development in cementitious materials in internal curing with modified superabsorbent polymer studied by NMR ,” *Microporous and Mesoporous Materials*, Vol. 125, No. 1-2, pp. 51-57, 2009.
- [25] Mechtcherine, V. et al.,” Modeling of water migration during internal curing with superabsorbent polymers,” *Journal of Materials in Civil Engineering*, Vol. 24, No. 8, pp.

Chapter 2 Properties of of superabsorbent polymers

1006-1016, 2012.

Chapter 3 Materials and experimental procedures

3.1 Materials

Ordinary Portland cement with a Blaine fineness value of 3310cm²/g is used. The compounds and chemical composition of the cement are given in Table 3-1 and Table 3-2. A commercial product of silica fume are used. The physical properties of silica fume is shown in Table 3-3. Two kind of fine aggregate is used. One is siliceous sand of which density and absorption are 2.62 g/cm³ and 0.40%, respectively. The other one is river sand of which density and absorption are 2.60 g/cm³ and 1.81%, respectively. A polycarboxylic acid type superplasticizer is used.

Seven types of SAP (A, B, C, D, 1, 2 and 3) are used. SAP-A, B, C and D are produced by aqueous polymerization while SAP-1, 2 and 3 are obtained by inverse suspension polymerization. As shown in Fig.3-1, SAP-A, B and C are irregular shape and contains greater particles, while SAP-D is smaller particle. SAP-1, 2 and 3 are almost mono-sized spherical powders. Tiny particles of SAP-2 and SAP-3 are gathered around large particles due to a surfactant. SAP-A, SAP-1 and SAP-2 are sieved to obtain two particle size ranges, large (300~600 μm) and small (150~300 μm). SAP-B and C are also sieved to obtain two particle size ranges, large (200~500 μm) and small (<200 μm). SAP-B, C, D and 3 of the original grading are also used. These properties of SAPs are summarized with notation of each SAP in Table 3-4.

Table 3-1 Chemical composition of cement (wt. %)

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO ₃	Cl ⁻
65.86	20.55	5.21	2.44	0.91	0.41	0.27	02.33	0.006

Table 3-2 Cement compounds (wt. %)

C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Total
62.2	12.1	9.68	7.42	91.4

Table 3-3 Physical properties of silica fume

Density (g/cm ³)	Specific surface area (m ² /g)	SiO ₂ (%)
2.20	20.00	90.80

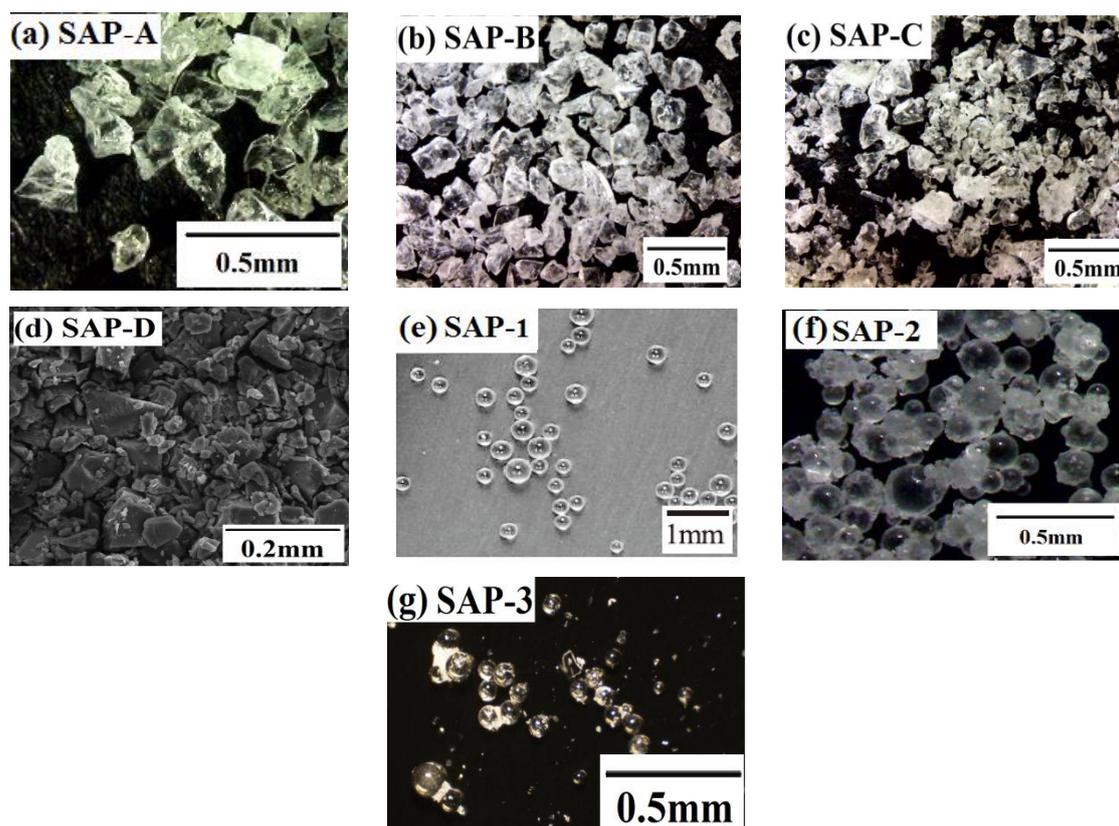


Fig.3-1 SAP particles at dry state

Table 3-4 Properties of SAP

SAP	Absorption capacity (g/g)	Particle size (μm)	Density (g/cm^3)
SAP-AL	10.0	300~600	1.45
SAP-AS		150~300	
SAP-BS	46.6	<200	—
SAP-BL		200~500	—
SAP-BN		Not sieved	—
SAP-CS	60.8	<200	—
SAP-CL		200~500	—
SAP-CN		Not sieved	—
SAP-D	28.0	Not sieved	—
SAP-1L	13.3	300~600	—
SAP-1S		150~300	—
SAP-2L	13.3	300~600	1.25
SAP-2S		150~300	
SAP-3	13.3	Not sieved	—

3.2 Experimental

3.2.1 Evaluation of water absorption capacity of SAP

(1) Tea bag method

The most popular measuring techniques to measure water absorption capacity of SAP is tea bag method. In accordance with JIS K 7223, the procedures are as follows:

1) Masses of about 0.20 g of dry SAP is put in a tea bag which had been pre-wetted in test solution. Nylon fabrics with sieve opening of 57 μm (255 mesh) are using for making the tea bag with 10 cm \times 20 cm oblong. The tea bag containing SAP is then hung in a 1L beaker filled with test solution.

2) In order to avoid carbonation, a foil is used for covering the beaker carefully. After 5 minutes, 15 minutes, 30 minutes, 60 minutes and 180 minutes immersion, the tea-bag with the SAP is weighed.

3) To remove weakly bound liquid and surplus, when immersion for specified period has finished, the tea bag with SAP is suspended in a laboratory making its bottom line get oblique for 10 minutes to drops off water. SAP cannot be squeezed to disturb the storage function of polymers.

The absorption capacity of SAP is calculated by the following equation:

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

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 tea 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) Modified tea bag method

RILEM TC-260-RSC proposes a modified tea bag method to simplify the steps and reduce the tea bag materials cost. In that procedure, excess water is removed by wiping with clothes, instead of hanging the tea bag. Put tea bag with SAP on a dry cloth and wipe with another dry cloth carefully and tightly for a short time of approximately 30 seconds to remove

excess solution. In addition, commercial tea bags with 6 cm×8.5 cm oblong are used instead of specific nylon fabrics. Thus mass of dry SAP is adjusted to 0.10 g for the modified tea bag method. The absorption capacity is measured when SAP is immersed in test fluids for 1, 5, 10, 30, 60 and 180 minutes according to RILEM TC-260-RSC.

The absorption capacity of SAP is also calculated by the Eq. (1).

(3) Graduated cylinder method

It is postulated that interparticle water is not properly evaluated by the tea bag method. As an easy and alternative method to evaluate the water absorption capacity of SAP instead of the tea bag method, Jensen [1] has proposed a new method that uses a graduated cylinder.

Graduated cylinder method consists in measuring the volume change of a certain mass of loosely packed SAP as it absorbs water. The measuring principle and the measured quantities are indicated in Fig.2-2. The water absorption capacity at equilibrium is measured. The first measurement is done after 30min SAP immersion by terminating the stirring and waiting for SAP particles to settle by gravity. Then the evaluation of absorption capacity is tested every 30minutes until 180minutes. The test is carried out in the laboratory at a temperature of 20±2 °C and relative humidity of 60±5%, which is as the same as tea bag method. The absorption capacity of SAP is calculated by the following equation [1]:

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

Where K (g/g) is water absorption capacity of SAP, m_1 (g) is the mass of dry SAP which is

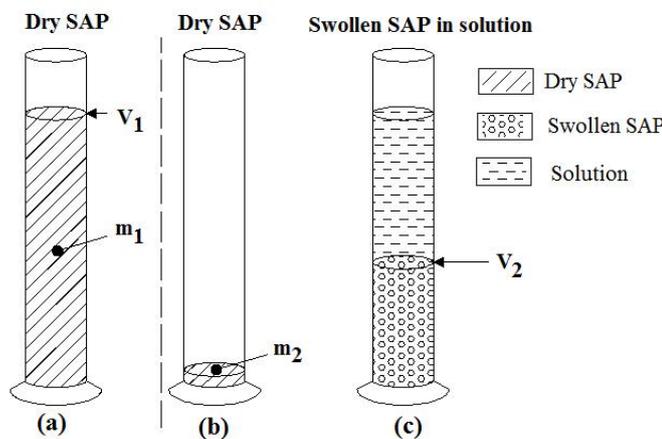


Fig.3-2 Determination of water absorption capacity of SAP by the graduated cylinder method [1]

filling a graduated cylinder to its maximum reading (Fig.3-2 (a)), V_1 (ml) is the volume of dry SAP which is filling a graduated cylinder to its maximum reading (Fig.3-2 (a)), m_2 (g) is the mass of about 0.10 g of dry SAP sample which is filled into a graduated cylinder (Fig.3-2 (b)), V_2 (ml) is the volume of swollen SAP after settling in the testing solution (Fig.3-2 (c)), ρ_{water} is the density of water, ρ_{SAP} is the dry, solid density of SAP, which is given in Table 3-2.

(4) Filtration method

In order to assess the possible sealing capacity of SAP particles, Snoeck [2] has proposed a filtration method to calculate water absorption capacity from the volume increase between the vacuum dried state and the saturated state. The process is as follow:

Dry SAP and test fluid of 100 ml are added in a beaker. In advance, a dummy test is performed to determine the amount of SAP due to freely swell to full extent in approximately 100 g of a test fluid. The swollen SAP and the test fluid are filtered after SAP immersion for the same prescribed time of 1, 5, 10, 30, 60 and 180 minutes as the tea bag method (Fig.3-3). The filter paper is saturated with the fluid before filtration, in order to ensure there is no influence of the filter paper. Filtration is continued until no drops are visible any more. The maximum filtration time is decided for a quarter of an hour to control the overall filtration, according to the advice by RILEM TC260-RSC. The filtration time is excluded in the total time. The test is carried out in the laboratory at a temperature of 20 ± 2 °C and relative humidity of $60 \pm 5\%$, of which condition is as the same as tea bag method. The absorption capacity of SAP is calculated by the following equation:

$$K = \frac{m_2 - m_3}{m_1} \quad (3)$$

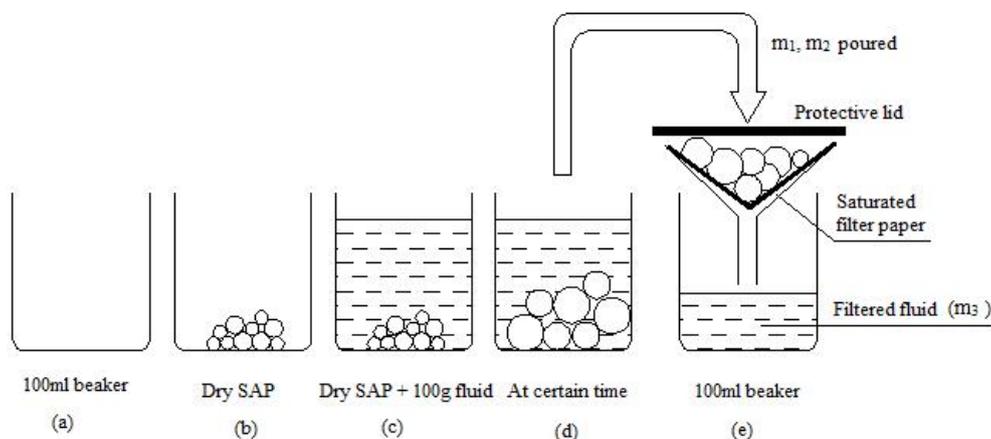


Fig.3-3 Procedure of the filtration method [2]

Where K (g/g) is water absorption capacity of SAP, m_1 (g) is the mass of dry SAP sample, m_2 (g) is the mass of test fluid added, which is approximately 100 g. m_3 (g) is the mass of filtered fluid (Fig.3-3 (e)).

3.2.2 Immersion solutions for water absorption capacity measurement of SAP

(1) De-ionized water

De-ionized water is used to observe the inherent ability of SAP, which may be relevant for potential incorporation with cement-based matrix. The pH-value of de-ionized water is about 6.9.

(2) The simulated pore solution

The simulated pore solution is a reproduction of the liquid phase of a cement pore solution that contains characteristic ions. Cement pore solution contains various ionic species, mainly of K^+ , Na^+ , Ca^{2+} , OH^- and SO_4^{2-} . 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 ($Ca(OH)_2$). Then it decreases slowly from about 3hours. Dissolution of alkali sulfates (K_2SO_4 and Na_2SO_4) into pore solution results 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 is determined. In addition, solutions 1, 2, 3 and 4 are 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.3-4. The

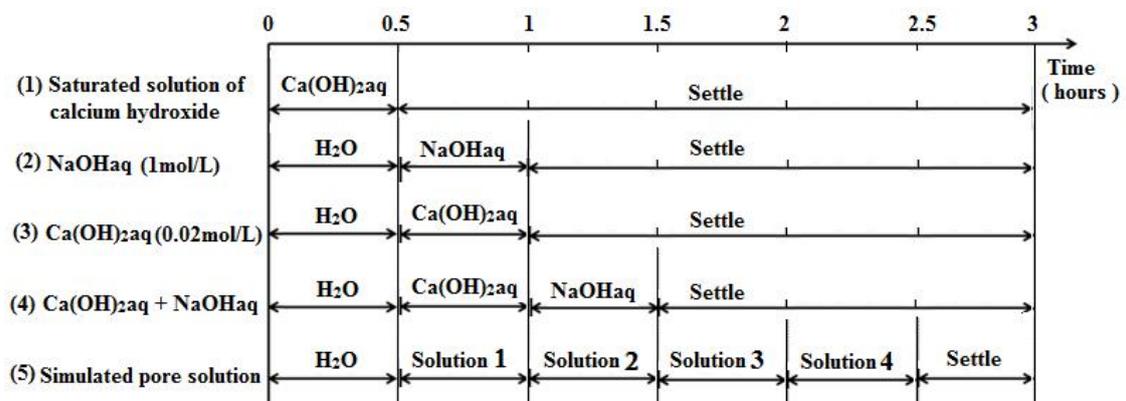


Fig.3-4 Sequence of pouring the alkaline solutions for the absorption capacity tests

Table 3-5 The molar concentration of cations in the 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

molar concentrations of cations in the simulated pore solution are indicated in Table.3-5.

(3) Cement slurry filtrate

Cement slurry filtrate is obtained by mixing ordinary Portland cement in de-ionized water and immersed 24 hours with continuous automated stirring. The suspension is subsequently filtered to remove residual solid cement particles. The water to cement ratio of cement slurry is 4.3, taking account of the current activity RILEM TC 260-RSC. The pH-value of the cement slurry filtrate is approximately 11.7.

3.2.3 Evaluation for mortars and cement pastes with SAP

(1) Mixing of mortars and cement pastes with SAP

A Hobart type mixer is used for mixing mortars and cement pastes in accordance with JIS 5201. Dry SAP is prepared for mixing. Mixing is done in the laboratory at a temperature of $20\pm 2^{\circ}\text{C}$ and relative humidity of $60\pm 5\%$.

(2) Setting

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

(3) Degree of hydration

The degree of hydration is determined from non-evaporable water. Based on the Powers

and Brownyard model [3], it is assumed that the ratio of the amount of non-evaporable water to the degree of hydration is constant at 0.23. Its non-evaporable water content w_n is determined by the loss on ignition. The degree of hydration α is calculated by the following equation [4]:

$$\alpha = \frac{w_n}{0.23} = \frac{(w_{105} - w_{1000})/w_{1000}}{0.23} \quad (4)$$

Where w_{105} (g) and w_{1000} (g) are the masses of the sample after drying at 105°C and 1000°C, respectively.

(4) Compressive strength

Compressive strength of mortars is determined by testing three 40×40×160mm prisms at the ages of 1, 7 and 28 days in accordance with procedures accordance with JIS R 5201. Specimens are demolded at 24 hours after casting, and then cured in water at 20°C until the prescribed ages for the test.

(5) Bleeding test

One of the primarily reasons have been proposed for early age expansions is uptake of bleed water after setting time. In order to investigate relationship between SAP addition and expansion at early ages, bleeding test is performed.

Bleeding test is conducted in this study in accordance with JIS A 1123. Cement pastes or mortars are poured into a graduated cylinder with the bottom diameter 100mm and height 100mm until the height of the specimen is 170±3mm. In order to evaluate the mass of bleeding water, bleeding water is transferred from the surface of specimen to a new cylinder with a pipet. The frequency measurement of bleeding water is increased by a 10 minutes interval within 60 minutes for accurately analyzing bleeding rate. After 60 minutes, the mass of bleeding water is tested every 30 minutes until no bleeding water is visible any more. Bleeding rate B_r is calculated by Eq. (6).

$$B_r(\%) = \left(\frac{B}{W_s} \right) \times 100 \quad (5)$$

Where B (kg) is the total mass of bleeding water at prescribed time interval, W_s (kg) is the mass of water in test sample.

(5) Length change test

Length change of mortars and cement pastes is measured by the corrugated tube method (Fig.3-5) in accordance with ASTM C1698-09 [5]. Specimens using special corrugated plastic molds of 420 mm in length and 30 mm in diameter are placed in the laboratory at a temperature of $20\pm 2^{\circ}\text{C}$ and relative humidity of $60\pm 5\%$. Length changes of the specimens are measured by laser displacement meters and digital gauges.

In a preliminary test, the initial setting time is determined using cement pastes with the same water to cement ratio as the mortar and cement paste. The initial setting time determined by Vicat needle penetration is used as the origin of length change, so called time zero ($t=0$).

(6) Drying shrinkage test

The drying shrinkage of mortar is measured based on the dial gauge method. The mortar is cast into cylinder acrylic mold of 390 mm in length and 30 mm in diameter. After 7 day curing in the laboratory at a temperature of $20\pm 2^{\circ}\text{C}$ and relative humidity of $60\pm 5\%$, which is the same as the length change test, the cylinder is demolded and the specimen is still placed in the laboratory for the further measurement. The initial gauge length of specimens is measured immediately after demolding, and consecutive readings of the change are measured using the dial gauge.

(7) Electrical resistivity test

Electrical conduction occurs primarily due to ion transport through the pore solution in a cement-based system. It is strongly dependent on pore solution conductivity, porosity and pore connectivity [6]. Therefore electrical resistivity measurements on fresh cement pastes and mortars

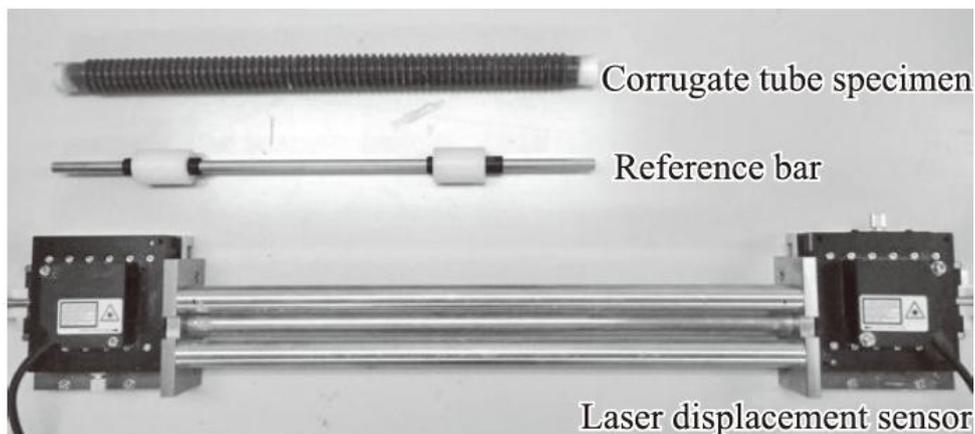


Fig.3-5 Measuring instruments of length change test

with SAP are performed to investigate early age characteristics.

The electrical resistivity is measured by the four electrodes method (Wenner method) in accordance with JSCE-K 562-2008 [7]. Mortars and cement pastes are directly placed into a cylindrical mold of 100mm in length and 50mm in diameter shown in Fig.3-6. Changes in the resistivity are continuously recorded up to twelve hours

Using the following equation, electrical resistivity ρ ($\Omega \cdot m$) is calculated:

$$\rho = \frac{V \cdot A}{I \cdot L} \quad (6)$$

Where V (V) is the potential difference between two current probes, A (m^2) is the sectional area of the mold, I (A) is current, L (m) is the distance between two current probes.

(8) Rheology test

Rheological properties of fresh concrete are related to hydration process and physicochemical interactions in the cement paste system at a plastic state [8]. Taking account of water absorption and/or water release from SAP in fresh and hardened concrete, the rheological properties are also influenced by the addition of SAP.

Plastic viscosity is measured with a commercial rheometer (Fig.3-7). The fresh cement pastes and mortars are tested with every 10 minutes after the water addition. After 1 hour, the fresh cement pastes are tested every 30 minutes until losing proper workability. Before each measurement, the specimen is 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

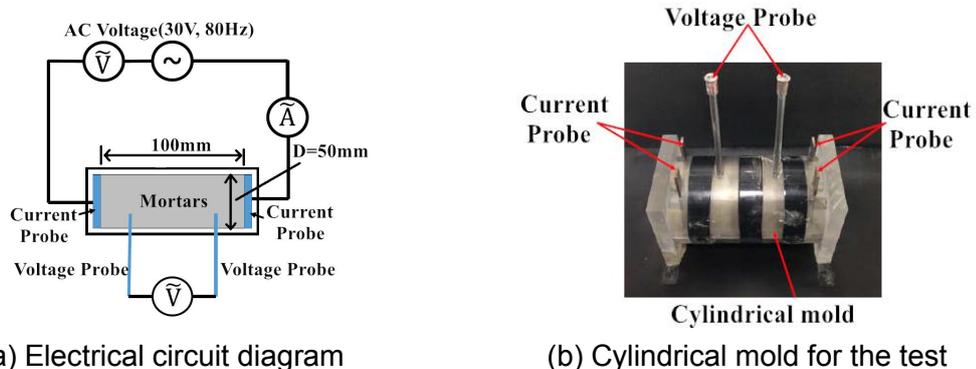


Fig.3-6 Schematic drawing of testing apparatus for the four electrodes method

the shear stress-shear strain rate curve is approximated by using linear regression analysis. The intersection of the linear regression line with the slope of the line provides the value of the plastic viscosity μ (Fig.3-8).

(10) Fluorescence microscope observation

Fluorescence microscopy is used to observe the bleeding water in mortars with SAP. The slices of 10 mm in thickness are prepared by cutting from the corrugate tube specimens after 7 days curing (Fig.2-5). The specimens are impregnated in ethanol for 24 hours to remove excess water. Then the specimens are impregnated with a low viscosity epoxy resin containing fluorescent dye. After the resin hardens at the room temperature, the slice is polished with abrasive papers and diamond slurry.

(11) Backscattered electron microscopy

Cement past cylinders of 100 mm in length and 50 mm are produced. At the age of 24 hours, and slices about 10 mm in thickness are cut from the central portions of the cement past cylinders for BSE image analysis [9]. The slices are dried by ethanol placement for 24 hours. Then the slices are impregnated with a low viscosity epoxy resin until the resin hardens at room temperature. The slices are finely polished with silicon carbide papers, and then the polished surfaces are meticulously finished with diamond slurry for a short time.

BSE images are acquired at the $500 \times$ magnification. Each image consists of 1148×1000 pixels, and one size of pixel is about $0.22 \mu\text{m} \times 0.22 \mu\text{m}$. A dynamic threshold method for several neighbors of pixels is used to obtain binary segmentation of capillary pores and unhydrated cement particles.

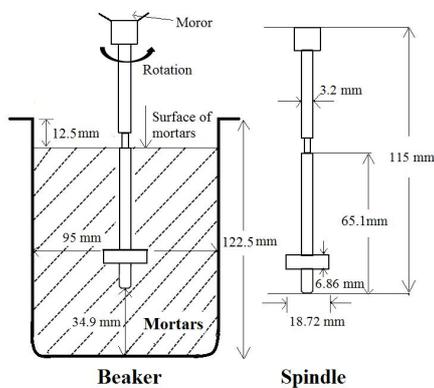


Fig.3-7 Schematic drawing of testing apparatus for the rheology test

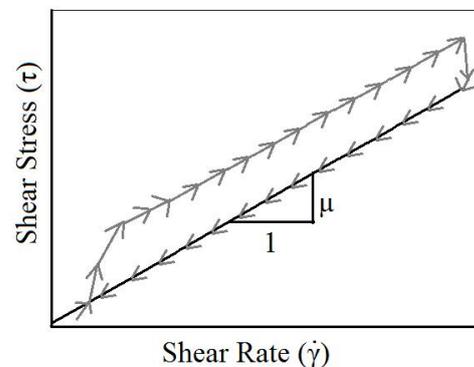


Fig.3-8 Schematic curve to determine plastic viscosity [9]

(12) Analysis of capillary pore spatial structure by two-point cluster function

Two-point cluster function reflects information about clustering in general continuum-percolation models [10]. Two-point cluster function gives the probability of finding two endpoints of line segment in the same cluster of capillary pore.

When capillary pores are considered as a spatial set P, the indicator function $I^{(P)}(x_i)$ ($i=1, 2$) of phase P may be defined as:

$$I^{(P)}(x_i) = \begin{cases} 1 & (x_i \in P) \\ 0 & (x_i \notin P) \end{cases} \quad (7)$$

The two-point correlation function $S_2^{(P)}(r)$ is defined as the probability of finding two endpoint x_1 and x_2 of a line segment in the same phase P (Fig.3-9 (a)). Two-point correlation $S_2^{(P)}(r)$ for the phase P is defined as follows:

$$S_2^{(P)}(r) = \langle I^{(P)}(x_1)I^{(P)}(x_2) \rangle = P\{I^{(P)}(x_1)=1, I^{(P)}(x_2)=1\} \quad (8)$$

Where the distance between two points is defined as $r = |x_1 - x_2|$. $P\{I^{(P)}(x_1)=1, I^{(P)}(x_2)=1\}$ is a probability that the two endpoints of a line segment hit the same phase P. $\langle \rangle$ means expectation.

Based on the two-point correlation function, the cluster function is obtained by judging whether the two points belong to the same cluster or not. As shown in Fig.3-9 (b), the cluster function gives the probability that a line segment of length r is fully on the one cluster, or the two endpoints of a line segment is on the one cluster.

In this study, a template with eight radial directions is used for the BSE images for calculation of two-point cluster functions [11]. As shown in Fig.3-10, the radial template with is put on a binary image. Whether both the endpoints hit the same phase or not, is determined by numerical operations. Then the template is moved to a different grid-point. It is repeated to

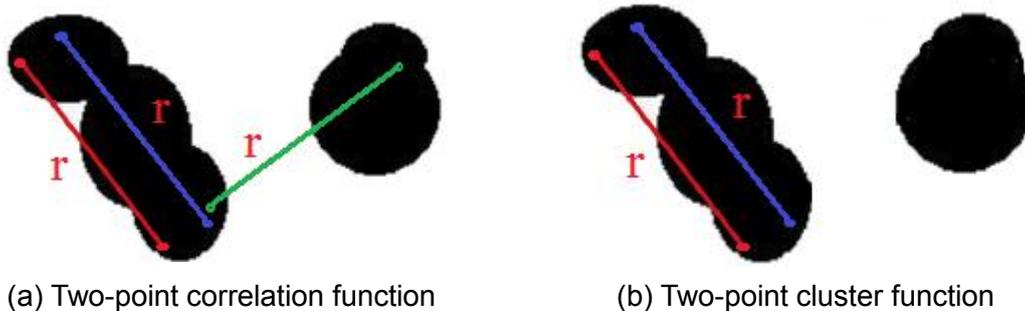


Fig.3-9 Schematic representation of correlation functions

Chapter 3 Materials and experimental procedures

acquire plenty of samples statistically for a specific length r by putting the template at different positions. Next, the radial length r is changed and the same steps as explained above is repeated. Probability that two endpoints of the segment probe hit the same cluster is also calculated by the numerical operations on the image.

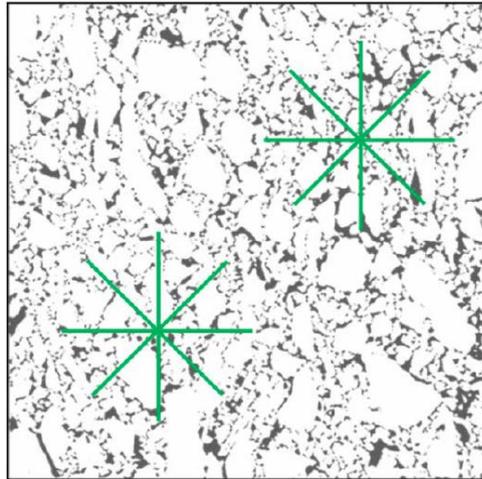


Fig.3-10 Radial Templates to compute two-point cluster function [12]

REFERENCES

- [1] Jensen, O.M.,” Water absorption of superabsorbent polymer in a cementitious environment,” International RILEM Conference on Advances in Construction Materials Through Science and Engineering, pp. 22-35, 2011.
- [2] Snoeck, D. et al.,” Visualization of water penetration in cementitious materials with superabsorbent polymers by means of neutron radiography,” Cement and Concrete Research, Vol. 42, No. 8, pp. 1113-1121, 2012.
- [3] Powers, T. C.: Physical properties of cement paste, 4th International Symposium on the Chemistry of Cement, Washington, D.C., 1962, U.S. Department of Commerce, National Bureau of Standards Monograph 43, Vol.2, pp.577-613, 1962.
- [4] Mouret. M., Bascoul. A. and Escadeillas. G.,” Study of the degree of hydration of concrete by means of image analysis and chemically bound water,” Advanced Cement Based Materials, Vol. 6, No. 3-4, pp. 109-115, 1997.
- [5] ASTM C1698-09: Standard Test Method for Autogenous Strain of Cement Paste and Mortar, 2009.
- [6] Sengul, O.,” Use of electrical resistivity as an indicator for durability,” Construction and Building Materials, Vol. 73, No. 30, pp. 434-441, 2014.
- [7] JSCE standards,” Test method for measuring resistivity of patching repair materials with four electrodes,” Sub-Committee on test methods and specifications for concrete, Committee on Concrete, Vol. 64, No. 3, pp. 427-434, 2008.
- [8] Mechtcherine, V., Egor, S. and Christof, S.” Effect of superabsorbent polymers (SAPs) on rheological properties of fresh cement-based mortars-Development of yield stress and plastic viscosity over time,” Cement and Concrete Research, Vol. 67, pp. 52-65, 2015.
- [9] Igarashi, S., Wakanabe, A. And Kawamura, M.” Evaluation of capillary pore size characteristics in high-strength concrete at early ages,” Cement and Concrete Research, Vol.35, No. 3, pp.513-519, 2005.
- [10] Torquato, S., Beasley, J. D. and Chiew, J. C.” Two-point cluster function for continuum percolation”. J Chem Phys, Vol. 88, No. 10, pp.6540-6547, 1988.
- [11] Igarashi, S., Chen W. and Brouwers, H.J.H.” Comparison of observed and simulated cement microstructure using spatial correlation function,” Cement and Concrete Composites, Vol. 31, No. 9, pp. 637-646, 2009.

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

4.1 Introduction

New application of SAP in concrete technology has been of a great interest, especially as additives for water control such as rheology modification. Therefore, it is essential to estimate SAP characters by certain measurement techniques before SAP is used for cement-based materials. However, practical and simple tests on SAP for concrete have not been standardized yet. More recently, RILEM has established a Technical Committee, RILEM TC 260-RSC “Recommendations for Use of Superabsorbent Polymers in Concrete Construction” (Chair: Prof. V. Mechtcherine, TU Dresden). Its main concern is to study a simple pre-test on SAP to disclose fundamental properties towards application in cement-based construction materials.

SAPs have the ability to absorb a significant amount water from the surrounding and to retain water within their structure without dissolving [1]. The absorption capacity of SAP are key aspects on their effects and performance in cement-based construction materials. The kinetics and sorption capacity of SAP depend on properties of the SAP, and its exposure environment [2]. In particular, the kinetics and sorption capacity of SAP in a highly alkaline solution are significant since pore solution in concrete has a quite high pH value.

Appropriate selection of exposure fluid is particularly important to determine the kinetics and sorption capacity with respect to the use of SAP in cement-based construction materials. De-ionized water, simulated pore solution and cement slurry filtrate are usually employed as the exposure fluid [3-5] as mentioned in Chapter. 3.

Several methods have been proposed to measure water absorption capacity of SAP. The tea bag method is frequently used to give a fast response of water absorption capacity of SAP. The absorption capacity evaluated by tea bag method is based on the mass of dry SAP in relation to the mass gain of the filled tea bag after it is removed from solution and drops off excess water by gravity. However, it is postulated that this method strongly depends on interparticle water. The water held by capillary forces between SAP particles cannot be totally removed. As an easy and alternative method, Jensen [2] has proposed a new method that uses a graduated cylinder. The method consists in measuring the volume change of a certain mass of loosely packed SAP as it absorbs water. The graduated cylinder method is considered as a useful way to evaluate water absorption capacity of SAP in cement environment [4]. However, it is sometimes difficult to see a rise in SAP height through the glass cylinder. On the other hand, in

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

order to assess the possible sealing capacity of SAP particles, Snoeck [5] has proposed a filtration method to calculate water absorption capacity from the volume increase between the vacuum dried state and the saturated state. He also has confirmed that the test result is not affected by the interparticle water. Therefore filtration method is considered as a promising technique to obtain a realistic value of absorption [6].

This chapter focuses on comparison of absorption capacity of SAP measured by the tea bag method, graduated cylinder method and the filtration method using de-ionized water, simulated pore solution and cement slurry filtrate. Effects of aqueous solutions with different concentrations of ions on the absorption and desorption behavior of different SAPs are investigated. The comparison between the results of absorption capacities is discussed from the viewpoint of retention of interparticle liquid on SAP particles during the test period. Furthermore, rheological behavior of fresh cement pastes and mortars with SAP is discussed in relation to the kinetics and sorption capacity of SAP.

4.2 Kinetics of water absorption and desorption of SAP measured by the tea bag method and the graduated cylinder method

This section focuses on water released from SAP due to osmotic pressure in highly alkaline solution. SAP-A and SAP-2 that are produced by the different methods are used. To evaluate it, two measurement techniques of the tea bag method and the graduated cylinder method are used. The procedures of the two method is provided in Sec. 3.2.1. The simulated pore solution which is mentioned in Sec. 3.2.2, is used to be absorbed in the absorption capacity tests. Effects of aqueous solutions with different concentrations of ions on the absorption and desorption behavior of different SAPs are investigated.

4.2.1 Swelling behavior of SAP evaluated by the tea bag method

Fig.4-1 shows changes in absorption capacity of SAPs with time of immersion in the saturated solution of calcium hydroxide. After they are dipped for 10 minutes, all the SAPs exhibit 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 [7]. However, when SAP-AL is immersed into the solution for a longer time, its absorption capacity decreases quickly, whereas the absorption capacity of SAP-2 decreases

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

gradually. The rate of reduction is not so great that most of absorption capacity is maintained in SAP-2.

Fig.4-2 also shows changes in absorption capacity of SAPs with time. In this test, to evaluate desorption properties at different alkaline conditions, all the SAPs are forced to absorb pure water in advance. Thus, the absorption capacity at the initial period of 30 minutes is much greater than the nominal value, which is given from the manufacturer (Table 3-4). Further, the maximum absorption capacity of any SAP sample is 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.4-2 (a)-(c), the addition of Na^+ shows 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 [8]. However, as for the SAP used in this study, it seems that impact of the presence of Na^+ cannot be ignored.

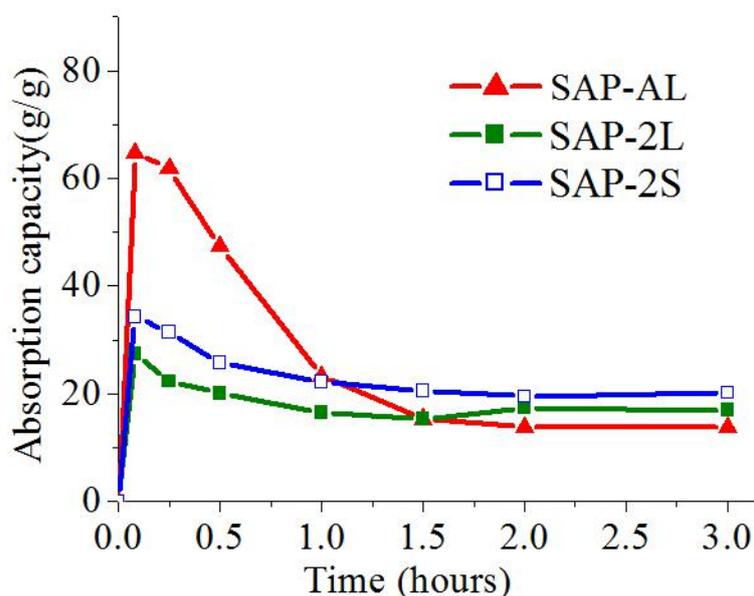


Fig.4-1 Change in absorption capacity in saturated solution of calcium hydroxide by the tea bag method

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

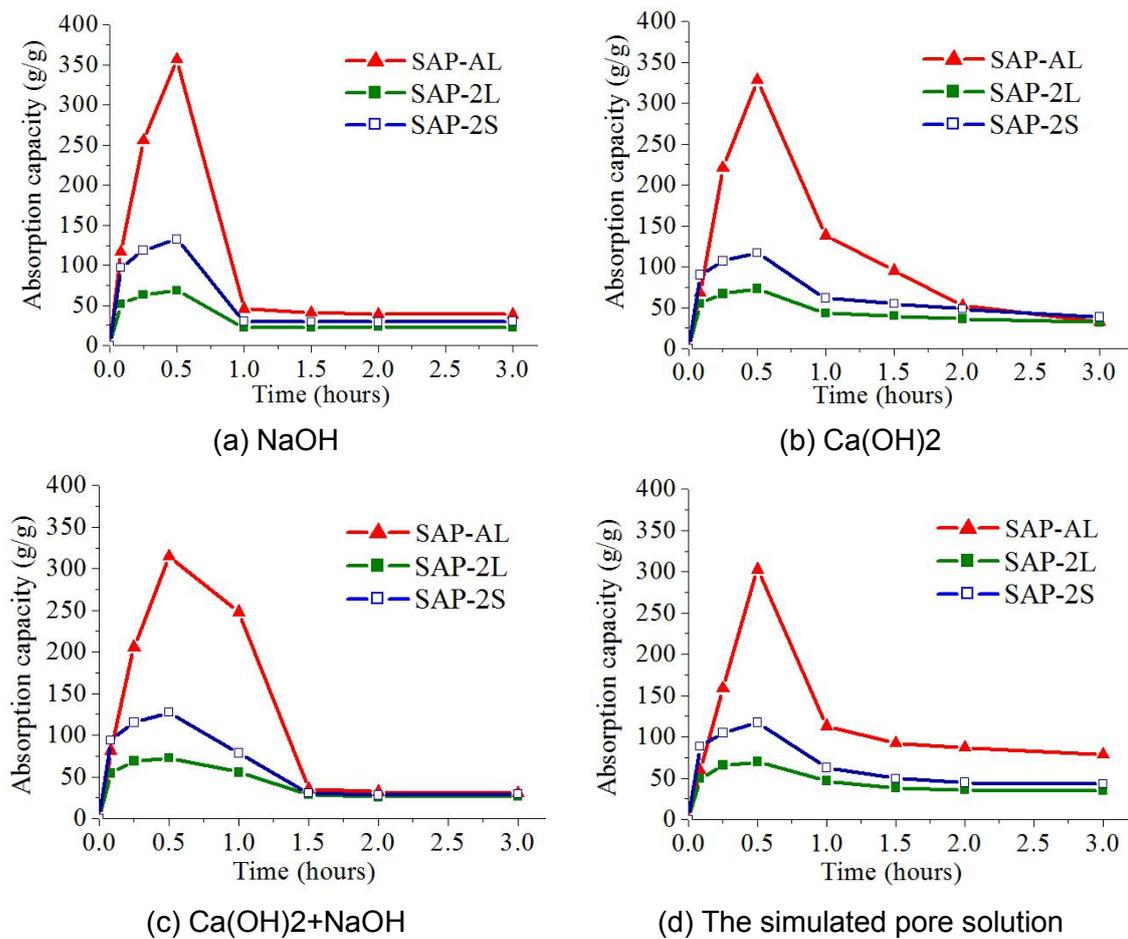


Fig.4-2 Change in absorption capacity with time evaluated by the tea bag method

4.2.2 Swelling behavior of SAP evaluated by the graduated cylinder method

Fig.4-3 shows changes in absorption capacity of SAPs with time. SAP-AL exhibits maximum absorption capacity at the value of 600g/g within 30 minutes, almost the double of the value obtained by the tea bag method (Fig.4-2). The maximum absorption capacities of SAP-2 obtained by the graduated cylinder are 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-2 is spherical. 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 contrast 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-2 is used,

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

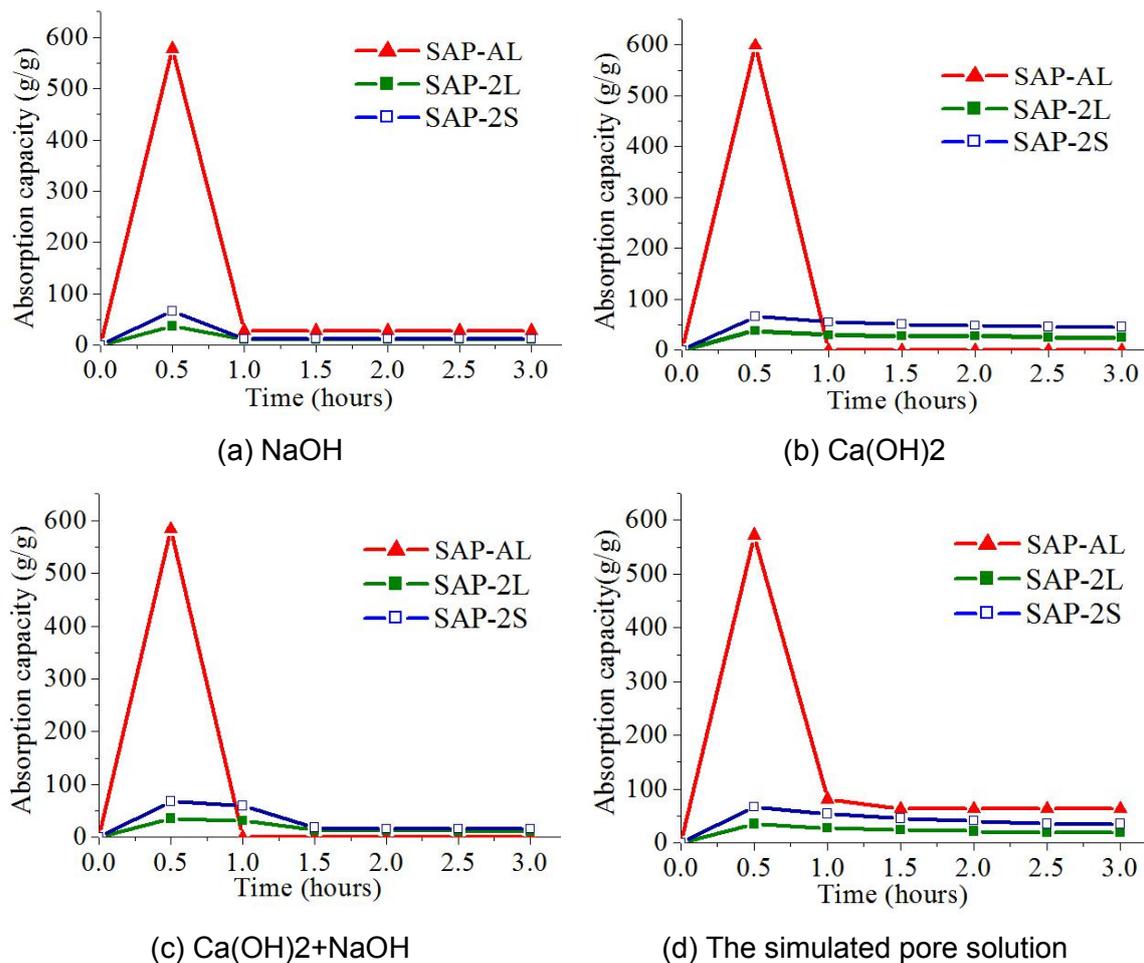


Fig.4-3 Change in absorption capacity with time evaluated by the graduated cylinder method

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 alkaline solutions and the simulated pore solution are added, the absorption capacity of SAP-AL always increases quickly, and then decreases rapidly. Eventually, equilibrium of absorption capacity is reached in 1 hour. SAP-2 showed a relatively stable and small value of absorption capacity than SAP-AL. In the tea bag method, the similar phenomenon is also observed (Fig.4-1 and Fig.4-2). Furthermore, when SAP-2 is used, the smaller SAPs, the relatively greater value of absorption capacity is observed. Luis [9] has reported that small particles of SAP have less absorption capacity since the surfaces of them are less active. The SAP he used was also produced by inverse suspension polymerization as well as SAP-2. Thus, experimental results in this study do not agree with them. In addition, when Ca^{2+} is added into solutions (Fig.4-3 (b) and (c)), SAP-AL almost releases 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 [8].

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

In view of all the results obtained by two measuring techniques, SAP-AL produced by aqueous polymerization that produces particles of irregular shape always show greater absorption capacity than SAP-2 obtained by inverse suspension polymerization with spherical shape. This result is not consistent with the properties provided by the manufacturer (Table 3-4). Thus, the absorption property of SAP must be interpreted carefully if detailed information on the measurement is not provided. The size of particles is also principal element with respect to the absorption kinetics [9]. 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 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.

4.3 Comparison of absorption capacity of SAP measured by the modified tea bag method and the filtration method

This section focuses on comparison of absorption capacity of SAP measured by the tea bag method and the filtration method using de-ionized water and cement slurry filtrate. The procedures of the two method and the immersion solution are provided in Sec. 3.2.1 and Sec. 3.2.2, respectively. SAP-B, SAP-C and SAP-3 are used in this section. The comparison between the results of absorption capacities is discussed from the viewpoint of retention of interparticle liquid on SAP particles during the test period.

4.3.1 Swelling behavior of SAP evaluated by the modified tea bag method

Fig.4-4 shows changes in absorption capacity of SAPs measured by the modified tea bag

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

method. After they are dipped for 10 minutes, all the SAPs exhibit rapid development of absorption capacities. When SAPs are immersed into de-ionized water (Fig.4-4 (a)), the maximum absorption capacity are observed at about 30 minutes and then changed little. When SAPs are immersed into the cement slurry filtrate (Fig.4-4 (b)), the maximum absorption capacity of any SAP sample is quite smaller than that in de-ionized water. The results are consistent with that measured by Snoeck [5]. The cations K^+ , Na^+ , Mg^+ and Ca^{2+} in cement slurry filtrate clearly result in the charge screening effect. Osmotic pressure which is results from the relative lower concentration of ions within the SAP polymer network compared to the external environment, leads to a reduced swelling of the SAP.

In view of the results obtained by the modified tea bag method, SAP-3 with spherical shape shows relatively consistent values of absorption capacity even if different solutions are used. They may be related to surface properties of SAP-3 particles that are produced by inverse suspension polymerization. All the particles with different sizes are produced from the solution. Effect of this process will be discussed later. Contrary to this, there are appreciable differences in absorption capacities between particle sizes in SAP-B. In spite of the same production method as SAP-B, little differences between the sizes are seen in SAP-C. Effect of particle sizes on absorption capacity depends on the products even if the same method is used to produce

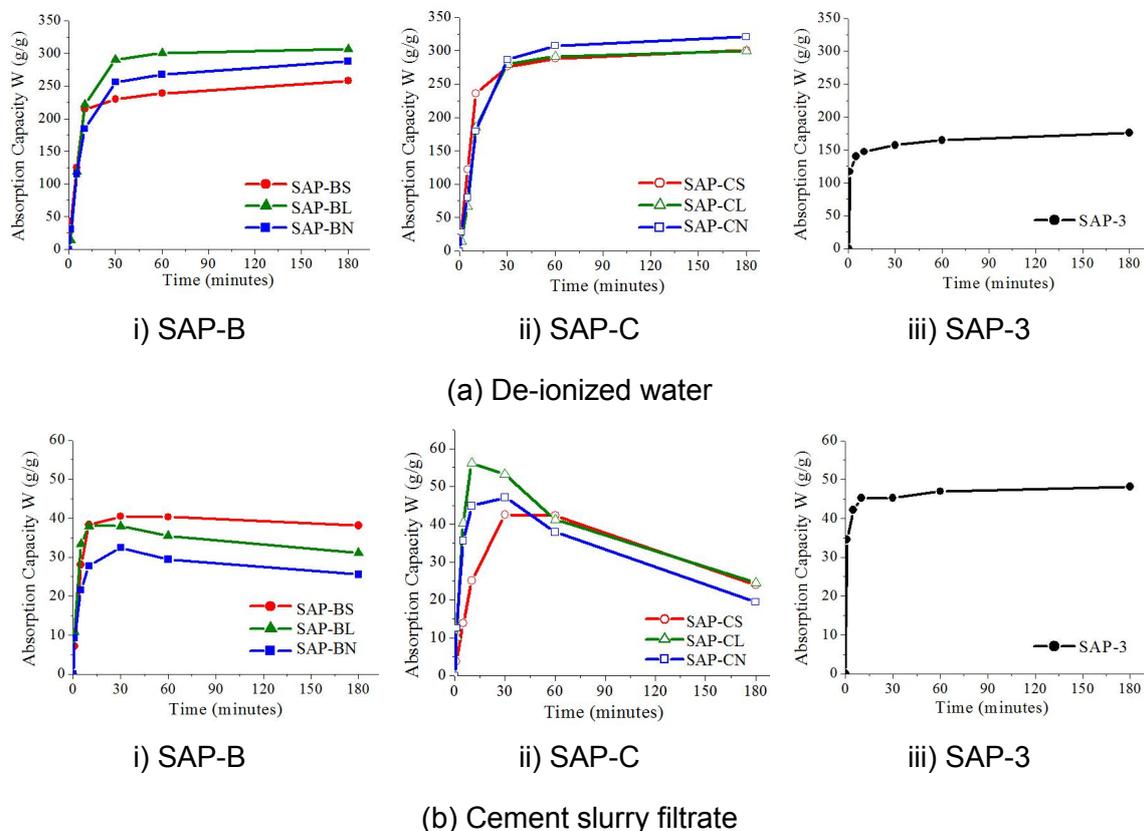


Fig.4-4 Change in absorption capacity measured by the modified tea bag method

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

SAPs [3].

4.3.2 Swelling behavior of SAP evaluated by the filtration method

Fig.4-5 shows changes in absorption capacity of SAPs measured by the filtration method. When SAP is immersed into de-ionized water (Fig.4-5 (a)), a similar trend is observed in SAP-B and SAP-C. SAP-BN and SAP-CN of the original grading show a greater absorption capacity than those of the large and small particles. Differences in the absorption behaviors are clearly seen in SAP-C whereas little differences are present in the modified tea bag method (Fig.4-4 (a) (ii)). The sensitivity to the particles sizes of SAP is also related to the measurement technique. Thus, the absorption property of SAP must be interpreted carefully not only from the data provided by the manufacture, but also by the proper measurement technical for the use in cement environment. When SAP is immersed in cement slurry filtrate (Fig.4-5 (b)), decreases in the absorption capacity are observed in SAP-AL, SAP-CN and SAP-3. A significant decrease in absorption capacity of SAP-C (Fig.4-4 (b) (ii)) is also observed. As mentioned above [8],

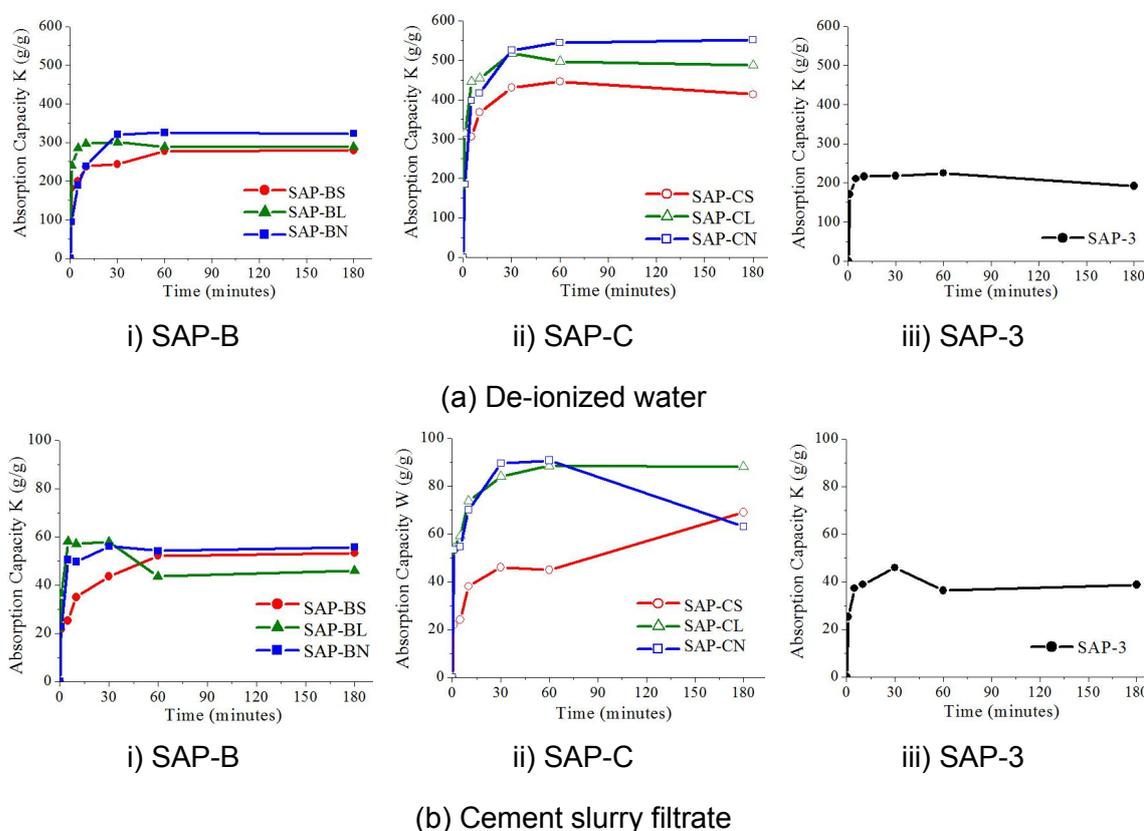


Fig.4-5 Change in absorption capacity measured by the filtration method

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

desorption from saturated SAP is mainly due to the diffusion of ions in the cement slurry filtrate of alkali solution.

In view of the results obtained by the filtration method, SAP-3 always shows the smallest value of absorption capacity, and SAP-C has the largest value of absorption capacity. This result is consistent with the properties provided in Table 3-4. Furthermore, it also corresponds to the result in Fig.4-4.

As found in Fig.4-4 also, SAP-3 with spherical shape that is produced by inverse suspension polymerization always shows a relatively stable absorption capacity than SAP-B and C. SAP of aqueous polymerization is macro-porous mass, which is produced by drying and pulverizing a gel-like elastic product. Dissolving reactants in water at desired concentrations, a fast exothermic reaction yields the gel-like elastic product with a large surface [10]. In the process of pulverization, the gel-like elastic product is pulverized and more new surfaces from its internal structure are exposed. This may be related to the difference in absorption capacity between particle sizes. In the process of inverse suspension polymerization, unique flowing properties of particles are provided [10]. This makes a better control of regulation of particle-size distribution. As a result of the process, SAP-3 particles could be less sensitive to the test fluid and the test methods.

4.3.3 Comparison of absorption capacity measured by the two methods

Fig.4-6 shows the relationship between absorption capacities measured by the two methods. The regression lines of linear fitting and correlation coefficients are given. When SAP is immersed into de-ionized water (Fig.4-6 (a)), it can be seen that the absorption capacities of SAP-B obtained from the two different methods are well correlated, and the regression lines have high correlation coefficients. This indicates that the modified tea bag method and the filtration method give very similar information about the absorption capacity of SAP-B immersed into de-ionized water. Compared with SAP-B, there are greater variation from linear regression in SAP-C and SAP-3. At the same time, the absorption capacity K measured by the filtration method is always appreciably greater than the absorption capacity W . SAP particles are easy to form agglomeration on the corner of a tea bag, which caused an obviously reduction in the contacting area of SAP particles and test fluid [11]. In practice, insufficient swollen SAP is observed in the tea bag. The insufficient swollen SAP may affect the smaller value of absorption capacity obtained by the tea bag method.

In addition, the increase in absorption capacity W for the testing period (ΔW) is obviously greater than that in absorption capacity K (ΔK) for SAP-BS and SAP-BL, while ΔW and ΔK

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

were very close for SAP-BN. The similar trend is also observed in SAP-C. The SAP without sieved showed a stable increase in absorption capacity than others. For SAP-3, the rate of increase in absorption capacity W to that in K is almost the same as SAP-BS and SAP-BL. Surfaces between SAP particles become larger with swelling. The larger particles, the more capillary water. The water between small particles is less since the packing of small SAP is denser than that of large SAP. The dense packing makes a narrow channel for reducing capillary water. The water held by capillary forces between SAP particles cannot be totally removed by the modified tea bag method, while almost excess water dropped off in the filtration method. Therefore, these tendencies may result in a large increase in absorption capacity during the test period measured by the modified tea bag method. In short, the increase in absorption capacity W during the test period seems to be contributed by the retention of interparticle liquid.

When SAP immersed into cement slurry filtrate (Fig.4-6 (b)), there are significant variations from linear regressions for SAP-B and C in contrast to that immersed into de-ionized water. However, for each SAP, the time-dependent change of absorption capacity shows a similar variation tendency whether SAP is immersed into de-ionized water or cement slurry filtrate. Thus, the tests with de-ionized water may be used for simple comparison of absorption capacity in cement environment while the absolute absorption capacity is quite different between the water and the cement slurry filtrate.

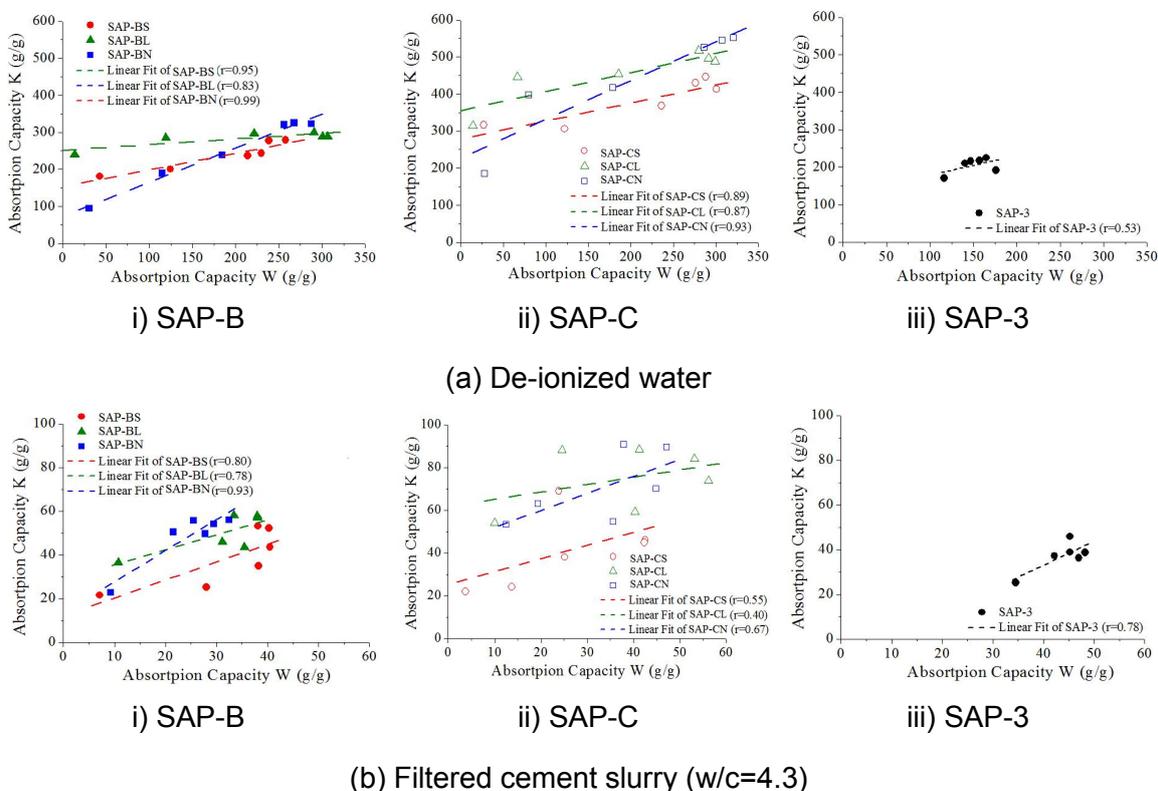


Fig.4-6 Correlation of absorption capacities measured the two methods

4.4 Effect of SAP on plastic viscosity of cement pastes at early age

4.4.1 Mixture proportion

Mixture proportion of cement pastes is given in Table 4-1. Cement paste and polycarboxylic acid type superplasticizer investigated in this section are already described in Sec. 3.1. Water to cement ratio of cement paste is 0.28. SAP-AL and SAP-2 are used. Dosage of SAP is determined to absorb 10% of mixing water. Therefore, the water absorbed by SAP to cement ratio is 0.028, so that the effective water to cement ratio of the bulk cement matrix is smaller than 0.28.

4.4.2 Results and discussion

Fig.4-7 shows time-dependent changes in plastic viscosity of the cement pasts. The reference specimens and ones with SAP-2L exhibit rapid increases in plastic viscosity right from the beginning of the measurements. Cement pastes with SAP-AL and 2S keep a stable value of plastic viscosity at first, and then start increasing rapidly about from 60 minutes. In other words, when SAP-AL and 2S are used, the time at which plastic viscosity start increasing is delayed. In particular, the cement pastes with SAP-AL show 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. [12] 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 4-1, the mixtures with SAP-AL and 2S show the longer final setting while almost the same initial setting is observed among the cement pastes. This fact

Table 4-1 Mixture proportion of cement pastes (mass fraction)

Mixes	W/C	W _e /C	C	W _e	W _{SAP}	SP	SAP	Initial	Final
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-2L(10%W)	0.28	0.252	1	0.252	0.028	0.0070	0.0022	3:42	4:46
SAP-2S(10%W)	0.28	0.252	1	0.252	0.028	0.0080	0.0022	3:19	5:34

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

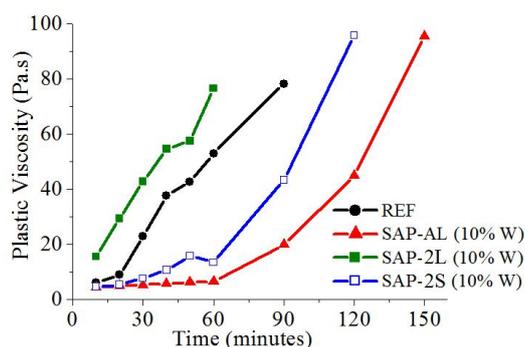


Fig.4-7 Development of plastic viscosity at early age

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 does 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.4-7 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 are recorded before the initial setting time when the water of SAP has 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-2L shows relatively stable and the least value of absorption capacity than SAP-AL and SAP-2S (Fig.4-2 and Fig.4-3). When SAP-2L absorbs 10% of mixing water, the freely available water in cement paste with SAP-2L is 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-2L is higher than that of the reference. Later, the freely available water is not supplemented effectively from SAP-2L. This causes rapid increase in plastic viscosity of cement paste with SAP-2L.

On the other hand, although SAP-2S absorbs almost the same amount of water as SAP-2L during mixing process, the value of plastic viscosity is 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 are different, the numbers

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

of SAP particles are different among the cement pastes. Therefore, their spatial distribution, in other words, the number densities of internal water reservoirs are different among the specimens at the beginning. In addition when the internal water is released, the initial distributions of moisture are also different among the specimens. This could affect the initial evolution of internal friction.

4.5 Effect of SAP on plastic viscosity of mortars at early age

4.5.1 Mixture proportion

Mixture proportion of mortars is given in Table 4-2. Cement paste and polycarboxylic acid type superplasticizer investigated in this section are already described in Sec. 3.1. The sand used here is river sand, which is also provided in Sec. 2.1. The water to cement ratio of mortar is 0.65. Dosage of SAP is determined to absorb 7.7% of mixing water. Therefore, the effective water to cement ratio in cement paste matrix is smaller than 0.65.

4.5.2 Results and discussion

It is common understanding that the absorption of pore solution by SAP is rapid and takes place in several minutes after mixing [7]. Mechtcherine et al. [13] have reported that the particle size distribution of SAP has been exhibited a considerable effect on the plastic viscosity at the first point

Table 4-2 Mixture proportion of mortars (mass fraction)

Mixes	W/C	W _s /C	C	S	W _e	W _{SAP}	SAP	Flow
REF-0.65	0.65	0.65	1	2	0.65	-	-	262
REF-0.60	0.60	0.60	1	2	0.60	-	-	221
SAP-BS(7.7%W)	0.65	0.60	1	2	0.60	0.050	0.001072	246
SAP-BL(7.7%W)	0.65	0.60	1	2	0.60	0.050	0.001072	255
SAP-BN(7.7%W)	0.65	0.60	1	2	0.60	0.050	0.001072	245
SAP-3(7.7%W)	0.65	0.60	1	2	0.60	0.050	0.003759	224

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

of time measured of 10 minutes after water addition to the mortars. Therefore, the fresh mortars are tested at 10 minutes after water addition.

Fig.4-8 shows values of plastic viscosity. As seen in REF-0.65 and REF-0.60, mortars with lower water to cement ratio exhibit significant greater values of plastic viscosity. The low content of solid cement particles in a mortar with the high water to cement ration loosens the suspension, which intensifies the flow ability of the material (Table 4-2). When SAP is used, the freely available water in mortars is less than that in REF-0.65, thus the value of plastic viscosity of mortars with SAP is higher than that of REF-0.65.

One the other hands, since the addition of SAP makes the effective water to cement ratio to similar to the reference specimens of REF-0.60, the plastic viscosity of mortars with SAP is lower than that of REF-0.60. This seems to be a logical case. When SAP is placed in hydraulically active suspensions, the absorption rate of SAP decreases since SAP must compete for water with cement and other fine solid particles.

However, differences of plastic viscosity between the mortars with SAPs are not as great as a whole. The results in this study do not agree with the result of Mechtcherine et al. [13]. All the SAPs reduce the internal friction of the mortar as gel-like water. Incorporation of different types of SAP does not lead to a great difference in plastic viscosity in mortars at the first time. However, as mentioned above, absorption and desorption properties depend on the types of SAP and time-dependent changes are expected. Therefore, it should be noted that the workability at 10 minutes after adding water could not be used for judging casting concrete at site if there is a time lag between the initial mixing and casting.

4.6 Conclusions

The kinetics and sorption capacity of SAPs and its effect on plastic viscosity are investigated. Major results obtained in this study are as follows;

- (1) The greater concentration of the alkaline solution, the lower the absorption capacity of the SAP.

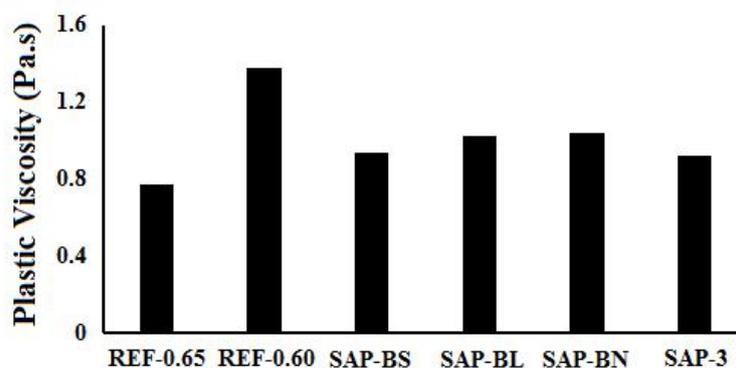


Fig.4-8 Comparison of plastic viscosity of mortars with different SAPs

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

The greater the kinetics of the liquid uptake, the rapider the kinetics of the liquid release. A similar variation tendency is observed between the modified tea bag method and the filtration method when SAP is immersed in de-ionized water and cement slurry filtrate. De-ionized water may be used as a simple exposure fluid for preliminary test to compare SAP intrinsic properties in cement environment.

- (2) SAPs produced by aqueous polymerization showed greater absorption capacity than SAPs obtained by inverse suspension polymerization. However SAPs produced by inverse suspension polymerization showed a relatively consistent behavior of absorption capacity than SAPs produced by aqueous polymerization.
- (3) Evaluation of absorption capacity measured by the modified tea bag method is smaller than that by the filtration method. The result of the modified tea bag method is easier to be affected by agglomeration of SAP particles, which seems to lead to insufficient swollen SAP. The increase in absorption capacity during the test period by the tea bag method seems to be contributed by the retention of interparticle liquid.
- (4) The similar variation tendency of absorption capacities of SAP could be obtained by the tea bag method and the graduated cylinder method. The graduate cylinder method is considered as a useful way to evaluate absorption capacity in cement environment.
- (5) 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. 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.
- (6) Differences of plastic viscosity at 10 minutes between the mortars with SAPs are not as great as a whole. It should be noted that the workability at 10 minutes after adding water could not be used for judging casting concrete at site.

REFERENCES

- [1] Jensen, O.M. and Hansen, P.F.,” Water-entrained cement-based materials I. Principles and theoretical background,” *Cement and Concrete Research*, Vol. 31, No. 4, pp. 647-654, 2001.
- [2] Jensen, O.M.,” Water absorption of superabsorbent polymer in a cementitious environment,” *International RILEM Conference on Advances in Construction Materials Through Science and Engineering*, pp. 22-35, 2011.
- [3] Luis, P.E.,” Superabsorbent polymers: On their interaction with water and pore fluid,” *Cement and Concrete Research*, Vol. 33, No. 7, pp. 717-724, 2011.
- [4] Hu, Q.Y., Yamazaki, K. and Shin-ichi Igarashi, S.,” Kinetics of water absorption and desorption of superabsorbent polymers and its effect on plastic viscosity of cement paste at early age,” *JCI*, Vol. 38, No. 1, pp. 2349-2354, 2016.
- [5] Snoeck, D. et al.,” Visualization of water penetration in cementitious materials with superabsorbent polymers by means of neutron radiography,” *Cement and Concrete Research*, Vol. 42, No. 8, pp. 1113-1121, 2012.
- [6] Snoeck, D. et al.,” Self-healing cementitious materials by the combination of microfibres and superabsorbent polymers,” *Journal of Intelligent Material Systems and Structures*, Vol. 25, pp. 12-24, 2014.
- [7] Mrzykowski, M. et al.,” Modeling of water migration during internal curing with superabsorbent polymers,” *Journal of materials in civil engineering*, Vol.24, No.8, pp.1006-1016, 2012,.
- [8] Zhu, Q. et al.,” Effect of ionic crosslinking on the swelling and mechanical response of model superabsorbent polymer hydrogels for internally cured concrete,” *Materials and Structures*, Vol.48, No.7, pp.2261-2276, 2015.
- [9] Luis, P.E.,” Superabsorbent polymers: On their interaction with water and pore fluid,” *Cement and Concrete Research*, Vol.33, No.7, pp.717-724, 2011.
- [10] Mohammad, J., Zohuriaan, M. and Kouros, K.,” Superabsorbent Polymer Materials: A Review,” *Iranian Polymer Journal*, Vol. 17, No. 6, pp. 451-477, 2008.
- [11] JIS K 7223:” Testing method for water absorption capacity of superabsorbent polymers” Japanese Industrial Standards Committee, 1996.
- [12] Sun, Z., Voigt, T. and Shah, S.P.,” Rheometric and ultrasonic investigation of viscoelastic properties of fresh Portland cement pastes,” *Cement and Concrete Research*, Vol.36, No.2, pp.278-287, 2006.
- [13] Mechtcherine, V., Egor, S. and Christof, S.” Effect of superabsorbent polymers (SAPs) on

Chapter 4 Kinetics of water absorption and desorption of SAP and its effect on plastic viscosity of cementitious materials

rheological properties of fresh cement-based mortars-Development of yield stress and plastic viscosity over time,” *Cement and Concrete Research*, Vol. 67, pp. 52-65, 2015.

Chapter 5 Early age autogenous deformation of mortars with low water to cement ratio

5.1 Introduction

Studies of autogenous deformations on cementitious materials with low water to cement ratio indicate that a period of early age expansion is often exhibited [1]. The impact of the expansion in mitigating autogenous shrinkage is considerable since differences in the initial expansion are reflected to subsequent differences in shrinkage at longer ages [2]. It should be noted that the expansion is often followed by considerable shrinkage. Mechanism of the expansion is not fully understood. Three primary reasons have been proposed for the expansion [3-5]: (1) thermal dilation, (2) deposition of hydration products and (3) uptake of bleed water after setting time. Cagnon et al. [6] measured the thermal deformations of aggregate, cement paste, mortar and a high performance concrete in 20°C-80°C, and reported a significant difference between coefficients of thermal expansion of cement paste and aggregate was observed. Bouny et al. [4] confirmed that calcium hydroxide appeared mainly as small crystals spread out among the C-S-H phase with low water to cement ratio by SEM observations, which could be responsible for expansion. Mohr and Hood [1] have recently pointed out that reabsorption of bleed water is the dominant mechanism of the expansion and that effects of thermal dilation and ettringite formation are minimal.

With the SAP particle used as an internal curing material in concrete to mitigate autogenous shrinkage [7], it also has been noticed that the addition of SAP sometimes results in large expansion at early ages [8]. The internal curing water released from SAP can be regarded as internal bleed water. It is important to clarify how bleed water and SAP addition affect fresh properties of cement-based material. Rheological properties of fresh concrete are related to hydration process and chemical interactions in the cement paste system at a plastic state. Furthermore, taking account of the purposeful water absorption and/or water release from SAP in fresh and hardened concrete, the rheological properties are also influenced by the addition of SAP [9]. The changes in rheological properties may also affect evolution of microstructure in concrete. As mentioned above, the released water may be involved in the hydration process of cement [10].

In order to investigate the evolution of microstructure immediately after placing concrete, electrical conductivity testing may be a useful way since electrical conduction occurs primarily due to ion transport through the pore solution in a cement-based system. Then it is strongly dependent on pore solution conductivity, porosity and pore connectivity [11]. They are

influenced by some factors such as water/cement ratios, cement types, chemical admixtures, and degree of hydration [12]. Therefore, electrical conductivity measurements on fresh cementitious materials are expected to provide useful information on microstructure in concrete at early ages [13].

The objective of this section is to investigate the effects of bleed water and SAP addition on the autogenous deformation behaviors at very early ages. Reabsorption of bleeding with superplasticizer and viscosity enhancement agent are discussed in relation to expansion first. Then, the evolution of microstructure in mortars with SAP is also discussed.

5.2 Influence of bleed water on early age volume changes in mortars with low water to cement ratios

5.2.1 Mixture proportion

Mixture proportion of mortars is given in Table 5-1. Cement paste investigated in this section is already described in Sec. 3.1. The sand used here is river sand, which is also provided in Sec. 3.1. A polycarboxylic acid type superplasticizer (SP) with 2% and 5% by the cement weight is added to mix. A viscosity enhancement agent (VE) with 0.056% by the cement weight is also added to mix.

Table 5-1 Mixture proportion of mortars (mass fraction)

Mixes	W/C	C	W	S	SP	VE	Flow	Initial setting (h:m)
SP=2%	0.28	1	0.28	2	0.02	0	223	5:06
SP=5%	0.28	1	0.28	2	0.05	0	268	7:39
SP=5%+VE	0.28	1	0.28	2	0.05	0.00056	239	15:20

5.2.2 Results and discussion

(1) Measurements of autogenous deformation

Fig.5-1 shows autogenous deformation that is recorded immediately after casting. The mortar specimen with 2% of the SP by the cement weight exhibits expansion during the period of 4 hours to 12 hour after water addition, then the system shrinks continuously. A significant expansion is observed from the beginning of the measurement in mortar with 5% of the SP. It is found that as the SP dosage increases, the observed expansion increases and develops earlier. However, expansion is not observed when the VE agent is added. Instead of expansion, the specimen shows a rapid shrinkage shortly after measurement by about 24 hours, then shows a plateau.

Fig.5-2 shows autogenous deformation after the initial setting time (i.e. Deformation is adjusted to zero at the time of initial setting). The initial setting time is provided in Table 5-1. A similar tendency of autogenous deformation is seen in the two specimens with 2% and 5% of the SP. It should be noted that the difference in autogenous deformations between the specimens with 2% and 5% of the SP at 60 hours is much smaller than that in Fig.5-1. The effect of the SP dosage on expansion is not distinct in this regard. In the mortar with the VE agent, the autogenous deformation is much smaller than that in Fig.5-1. However, it is still obviously found that the autogenous deformation in the mortar with the VE agent is greater than those of the mortars without the VE agent addition.

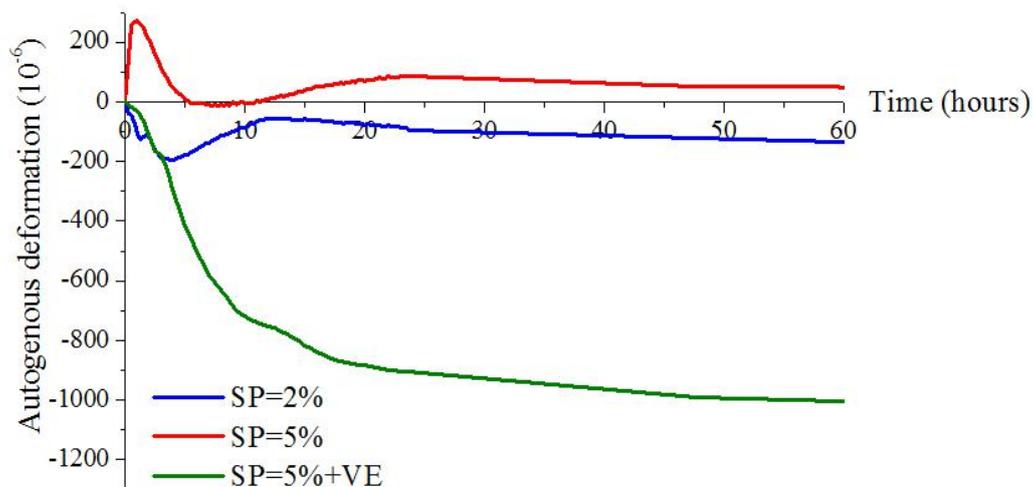


Fig.5-1 Autogenous deformation of mortars continuously recorded after casting

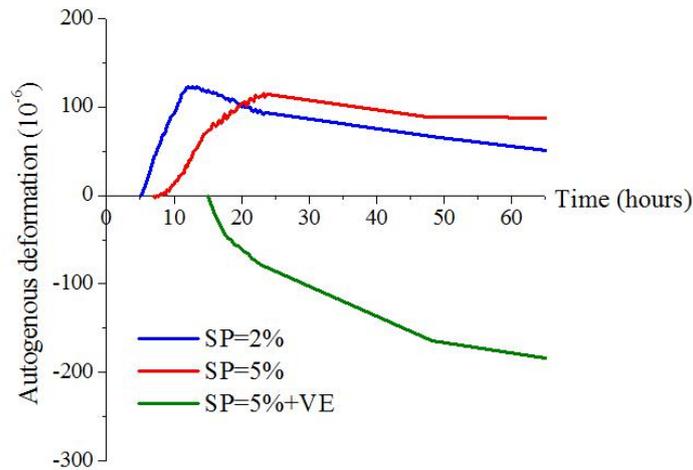


Fig.5-2 Autogenous deformation of mortars after the initial setting time

Fig.5-3 shows measurements of bleeding rates of mortars. By measuring the amount of bleed water accumulated on the specimen surfaces, it is found that when the SP is added, the mortars have a certain amount of bleed water. Meanwhile, the mortar with the VE agent have a negligible bleed water. When the SP of 2% is added to mortar, the bleeding rate increases quickly before 20 minutes and reaches a plateau after 40 minutes, due to no bleed water exist. The similar phenomenon is observed when the SP of 5% is added. The bleeding rate of mortar with 5% of the SP is almost triple the value of mortar with 2% of the SP.

External bleed water is observed for the mortar with the SP, which exhibited early age expansion. The measurements of autogenous deformation can be influenced by bleed water collecting on the mortar surface before setting. Bleed water is controlled by the VE agent, while bleed water is induced by the SP. The external bleed water is removed through the initial pore space of the mortar surface before the setting of cement, and then transformed into internal

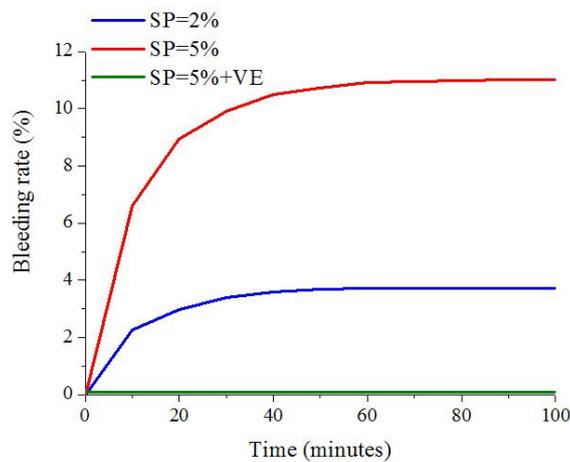


Fig.5-3 Bleeding rates of mortars

bleed water. After the setting, the bleed water may be reabsorbed as self-desiccation occurs, resulting in reduced autogenous shrinkage, or even expansion [5]. In addition, although the bleeding rate of the mortar with 2% of the SP is quite smaller than that of mortar with 5% of the SP (Fig.5-3), the expansion is not so different between the two mortars (Fig.5-2). Therefore, a little reduction of external bleed water may will not be enough to influence the entire expansion. One the other hand, it is noted that the time when expansion started increasing is quite different from the time of steep increasing bleed water in mortar surface and the time when the surface bleed water is removed. It may show that reabsorption of bleed water also influences autogenous deformation for long term. Even in the period after all the bleeding water has been consumed, the autogenous deformation may also be affected.

(2) Effect of bleed water on early age properties of mortars

The degree of hydration of cement in mortars is shown in Fig.5-4. At 6 hours, there are slight differences in the degree of hydration between the mixtures. After 12 hours, the degree of hydration of the mortar with 2% of the SP is greater than that of others until 24 hours. It may explain difference in the autogenous deformation, especially expansion due to reabsorption of bleed water. The reabsorption of the bleed water may accelerate the hydration of cement so that internal solid skeleton has formed earlier in the cementitious system, which results in the earlier expansion behavior (Fig.5-2). However, the excess addition of the SP cannot lead a higher degree of hydration and expansion. It shows a similar degree of hydration to that of the mortar with the VE agent.

The electrical resisivities of mortars are shown in Fig.5-5. All the mixtures exhibit a similar tendency in electrical resistivity with time. The electrical resistivity slowly drops at first

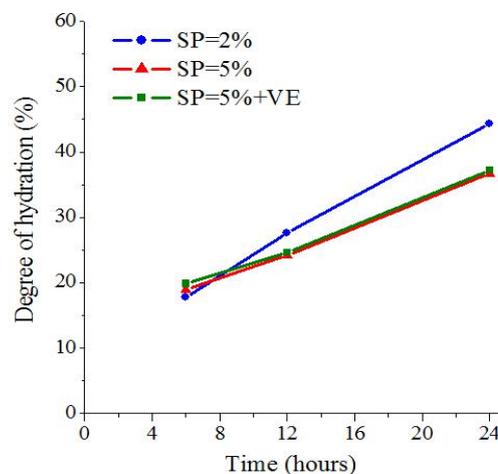


Fig.5-4 Changes in the degree of hydration of cement in mortars

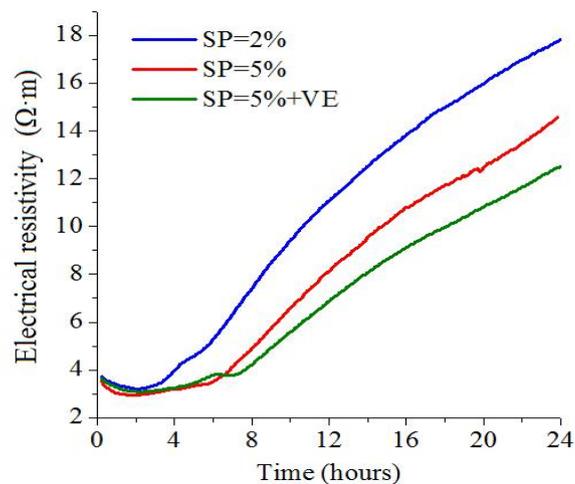


Fig.5-5 Development of electrical resistivity in mortars with SAPs

and then gradually increases with time. It should be noted that the mortar with 2% of the SP has a greater electrical resistivity than the mortars with 5% of the SP. The development of the electrical resistivities corresponds to the degree of hydration (Fig.5-4). Pore structure and connectivity are major factors that control the electrical resistivity [14]. The degree of hydration directly relates to the fraction of the hydration products and porosity in a hydration system [13]. For the mortar with the SP, the times when the electrical resistivity started increasing are almost coincident with the initial setting time. Chemical shrinkage and reabsorption of the bleed water by hydration products occur simultaneously after setting. When the amount and connectivity of pores are reduced, the internal solid skeleton is expected to be formed during the early of hydration of cement. As a result, higher electrical resistivity is obtained. On the other hand, the time when the increase in electrical resistivities for the mortar with the VE agent occurs is almost same to that of the mortars with 5% of the SP. And a smaller electrical resistivity is observed for the mortar with the VE agent than that of the mortar with 5% of the SP, even they have a quite similar degree of hydration of cement.

Except for controlling of bleeding, the VE agent has ability to build sufficient viscosity by enhance the water retention capacity of the paste. Fig.5-6 compares the increased plastic viscosity. The mortar with the VE agent exhibits a rapid increase in plastic viscosity right from the beginning of the measurements, since the use of the VE agent in cement- based system reduces the amount of free water available for lubrication of the paste and increases its viscosity at very early age [15]. Meanwhile, at first the mortars with the SP keep stable values of plastic viscosity, then start increasing. The mortar with 2% of the SP shows an earlier increase than the mortar with 5% of the SP. Its tendency is consistent with the degree of hydration (Fig.5-4). As for the electrical resistivity, on the one hand, the mortar with the VE agent can enhance cohesiveness of cement-based system even before the setting. On the other hand, a delay in the

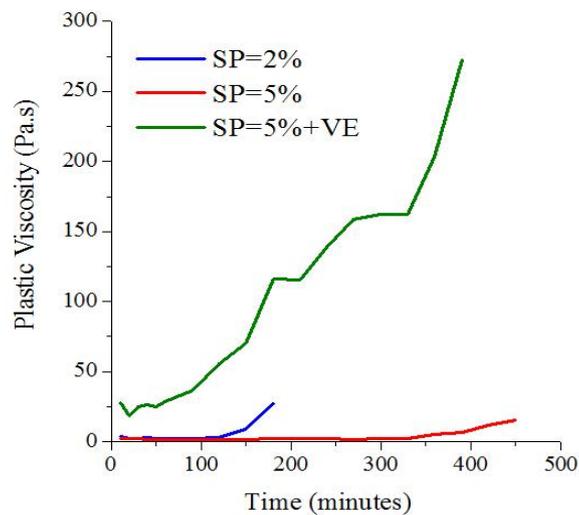


Fig.5-6 Development of plastic viscosity at early age

initial setting time is observed. Therefore, the electrical resistivity increases earlier before the setting. Besides, there must be some differences in the microstructure between the mortars with the VE agent and 5% of the SP, even they have the similar degree of hydration of cement.

(3) Fluorescence microscope observation of internal bleeding

Fluorescence microscope images of mortars at 7 days are shown in Fig.5-7. The mortars with the SP have higher fluorescent light intensity, while it is not observed in the images of the mortar with the VE agent. In other words, there are porous regions around aggregate particles for the mortars with the SP, and the porous regions is related to internal bleeding. Meanwhile no internal bleeding is observed in the mortar with the VE agent. Incorporation of the VE agent can reduce the free water in cement-based system. Furthermore, the mortar with 5% the SP has a larger area of fluorescent light, which may mean there are more inter bleeding then that of mortar with 2% the SP. The phenomenon is consistent with the external bleeding of mortars (Fig.5-3).

The sources of bleed water may be divided into three part: the one is absorbed water in the aggregates, the second is internal water which is trapped internally under aggregate particles, and the third is the visible external bleed water which passed through the initial pore space of the mortar surface. The visual external bleed water may affect the sources of internal bleeding significantly. Besides, it should be noted that the specimens for fluorescence microscope observation have been cured for 7 days, but the internal bleeding is also observed. It means porous region due to the internal bleeding has been left in cement-based mixture for a long time, which may also influence autogenous deformation for long term as mentioned before. However,

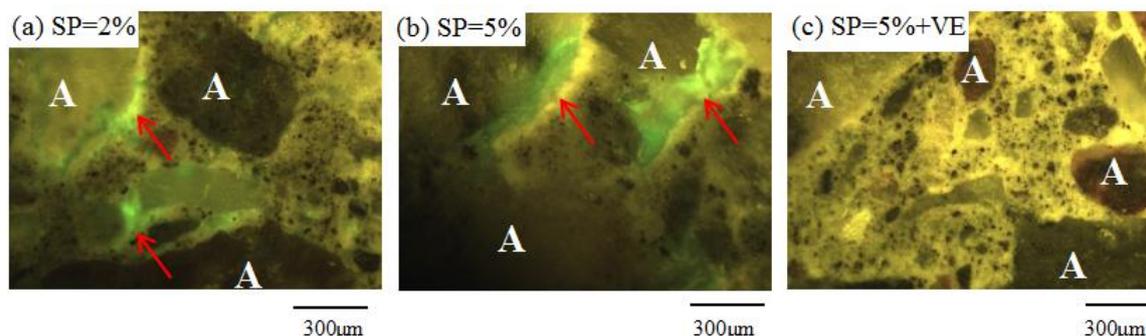


Fig.5-7 Fluorescence microscope image of mortars at 7 days
(A: Aggregates, Red arrow: bleed water)

the expansion is not as different for the two mortars with the SP as mentioned above (Fig.5-2). The consumed part of internal water, which is used for compensating self-desiccation, can be regarded as the same amount, due to the similar expansion. Another part of internal water is not consumed as observed in Fig.5-7. In other words, there exists a large area in which self-desiccation could not be compensated by the internal water [16]. One of the reason may related to the nonuniform distribution of internal water within the whole cement-based mixture. Furthermore, the internal water cannot migrate from internal water reservoirs to the surrounding maturing cement paste, therefore it cannot interact with cement pastes successfully [18].

5.3 Effects of SAP on expansive behavior of mortars at early ages

5.3.1 Mixture proportion

Mixture proportion of mortars is given in Table 5-2. Using the equation proposed by Jensen and Hansen [7], the amounts of SAP for the internal curing at W/B of 0.28 is determined. The fine aggregate used here is siliceous sand. A commercial product of silica fume is also used. SAP-A and SAP-1 supplied from different manufactures procedure are used.

Table 5-2 Mixture proportion of mortars (mass fraction)

Mixes	W/B	C	SF	S	SP	SAP
Control	0.28	1	0.094	1.89	0.017	-
SAP	0.28	1	0.094	1.89	0.017	0.003

5.3.2 Results and discussion

(1) Effect of SAP addition on autogenous shrinkage

Autogenous deformation behavior of mortars using each SAP is shown in Fig.5-8. The control mortars show noticeable deformations due to shrinkage after the initial setting to 1 day. After 1 day, the hydration may slow down and effects of chemical shrinkage on the length change are reduced due to the formation of internal solid skeleton [17]. In contrast to the control mortars, mixtures with SAP exhibit expansion from the beginning to 1 day. It is clearly found from Fig.5-8 that the early age expansion is related to the presence of internal water. The large particles of SAP-AL and SAP-1L result in greater initial expansion than those with the small particles of SAP-AS and SAP-1S. Periods of the expansion continue longer when the large SAPs are used. The addition of SAP greatly reduces subsequent shrinkage. The magnitude of the expansion and the extent of shrinkage reduction depend on the size of SAPs. Differences in the initial expansion are reflected to subsequent differences in shrinkage at longer ages. A large part of the reduction in autogenous shrinkage results from the initial expansion.

In view of the autogenous deformation curves for the mortars with the SAPs, the internal curing by SAP is only effective at an early stage. Then the autogenous shrinkage of the SAP mixtures develops nearly parallel to the control without SAP after the initial expansion. The autogenous shrinkage behaviors of the mortars with SAP should be discussed in relation with the time when the internal water is released from the SAP. Most of the SAPs produced as internal curing materials release the absorbed alkaline water to the surrounding cement matrix at very early ages [9]. This occurs irrespective of self-desiccation of the surrounding matrix. It may be an intrinsic property of SAP [9].

Changes in absorption capacity of SAPs with time of immersion into saturated calcium

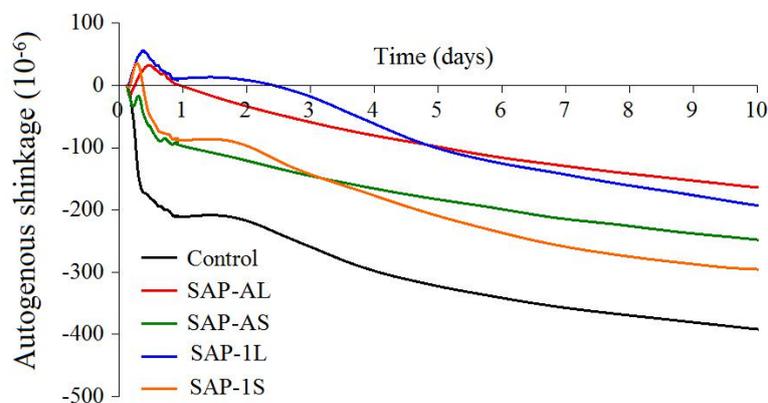


Fig.5-8 Autogenous deformation of mortars with SAP

hydroxide solution are shown in Fig.5-9. After they are dipped into the solution for ten minutes, all the SAPs exhibit their maximum absorption capacity. 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 [18]. However, when they are immersed into the solution for a longer time, their absorption capacity decreases quickly. The absorption capacity at 1 hour is less than a half of the initial capacity in all the SAPs. The smaller SAPs, the earlier decrease in absorption capacity is observed. Therefore, the small SAP in the actual mortars could also release the internal water at very early ages whereas the environmental condition in mortar is different from that of the tea-bag method. The release of the internal water from the large SAPs takes place slowly compared to small SAP (Fig.5-9). The released water from SAP affects the expansion at very early ages since it is regarded as internal bleed water [5]. Eventually, when the internal curing water is consumed or confined, its effect on the expansion decreases so that an apparently change from expansion to shrinkage is observed. Then the increase in autogenous shrinkage of the SAP mortars proceeds at the same rate as that of the control mortars (Fig.5-8). As for the mortars with large SAPs, expansion continues longer. This behavior may be related to the desorption rate of SAP. When the large SAPs are used, it exhibits a smaller rate of desorption, which affects the longer period of expansion (Fig.5-8).

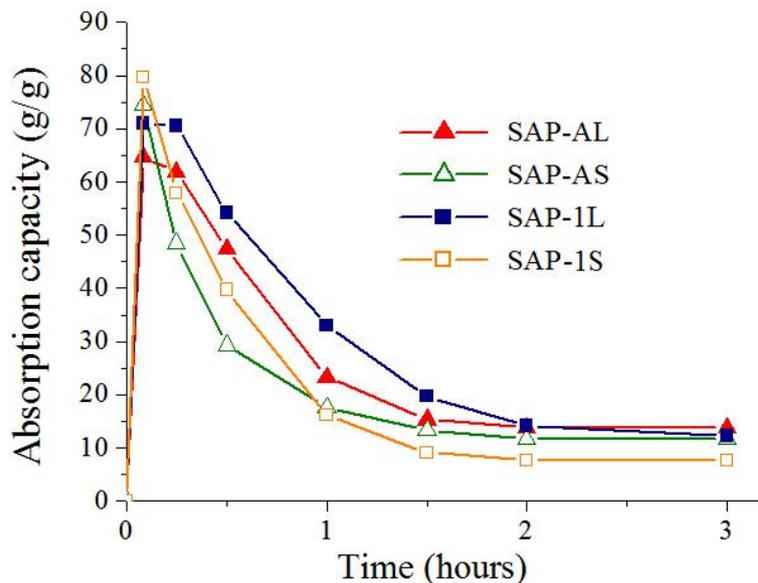


Fig.5-9 Change in absorption capacity with time immersed into saturated calcium hydroxide solution

(2) Effect of SAP addition on electrical resistivity

The electrical resistivities of mortars are shown in Fig.5-10. All the mixtures exhibit a similar tendency in electrical resistivity with time. The electrical resistivity slowly decrease at first and then gradually increases with time. At the beginning, the control mortars show a greater electrical resistivity than the SAP mortars, but a slow rise with time results in a smaller resistivity than mortars with the large particles of SAP at long ages. The electrical resistivity of the mortars with the large SAPs is greater than that of the mortars with the small ones at 10 hours. It should be noted that the times when the resistivity begins to increase in the SAP mortars are about 1 hour earlier than the control mortars. Setting times are also shown in Fig.5-10. The times when the resistivity of the SAP mixtures begin to increase are almost the same as the initial setting time while it is between the initial and final setting in the control. The initial setting time is close to the end of the dormant period. In this study, effect of pore solution composition on electrical resistivity is not considered since all the mixtures have the same W/B. The electrical resistivity development with time still reflects the hydration process and evolution of capillary pore networks in mortars [19]. At the acceleration period after the initial setting time, chemical shrinkage and reabsorption of bleed water by hydration products occur simultaneously. Internal relative humidity is kept high by internal curing. Effects of the internal water from the SAPs are dominant so that the expansion is observed in the SAP mortars. Thus the hydration of cement can proceed so that internal solid skeleton is expected to be formed earlier in the SAP system. This results in the early increases in electrical resistivity (Fig.5-10).

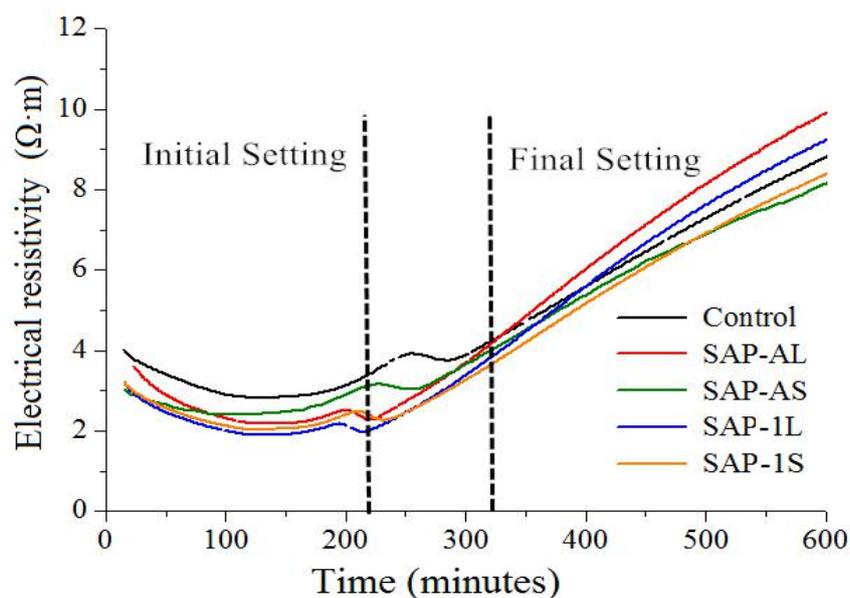


Fig.5-10 Development of electrical resistivity in mortars with SAPs

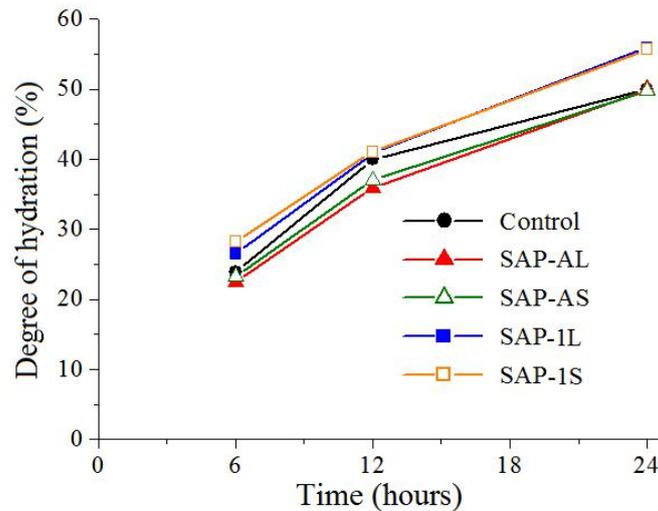


Fig.5-11 Changes in the degree of hydration of cement in mortars with SAPs

Fig.5-11 shows the degree of hydration. Mixtures with SAP-1 show higher degrees of hydration than that for the control mixture. For the mixtures with SAP-A, the degree of hydration is comparable to the control mixture. However, differences in the degree between the mixtures are relatively small on the whole, whereas electrical resistivities in the SAP mortars start to increase earlier than the control (Fig.5-10). This fact suggests that autogenous shrinkage behaviors and the development of electrical resistivity in the SAP mortars cannot be explained simply from the amount of hydration products and their uptake of bleed water. In addition to the uptake of bleed water by hydration products, some other factor to change expansive behaviors in the SAP mortars should be taken into account.

(3) Effect of SAP addition on plastic viscosity of fresh mortars

Fig.5-12 shows time-dependent changes in plastic viscosity of fresh mortars with and without SAP. At first they keep a stable value of plastic viscosity, then start increasing rapidly. The control mortar exhibits a little higher plastic viscosity right from the beginning of the measurements. When SAP is used, the time at which plastic viscosity starts increasing is delayed. The mortars with SAP-1 show a remarkable increase in plastic viscosity at 120 minutes. In contrast to this, gradual increase is observed for the mortars with other SAPs. Furthermore, the plastic viscosity in the mortars with SAP-1 depends on its particle size whereas there is no difference in the viscosity between the mortars with SAP-AL and SAP-AS. It should be noted that these changes in the plastic viscosity are recorded before the initial setting time. In fact, they are observed in the periods when the internal water of SAP has released already. In particular, it should be also noted that SAP-1L absorbs water as quick as other SAPs, but it

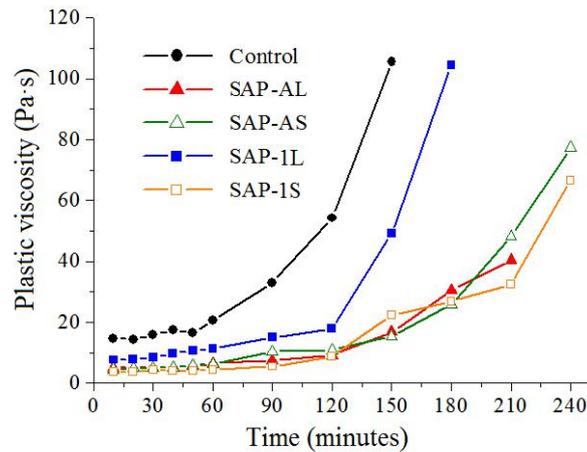


Fig.5-12 Development of plastic viscosity at early age

keeps it longer than the others (Fig.5-9).

Fig.5-12 clearly suggests that there must be some differences in microstructure between the mixtures with different SAPs even if it is in the dormant period in the hydration of cement. Basically, plastic viscosity reflects internal friction of a material. Therefore those differences in the internal friction result from the released water from SAP since it occurs during such a very early age. All the SAP mortars in this study have almost the same amount of internal water. However, the numbers of SAP particles are different among the mortars since the particle sizes of SAP are different. Therefore, their spatial distribution, in other words, the number densities of internal water reservoirs are different among the specimens. Thus when the internal water is released at very early ages before the initial setting time, the initial distributions of moisture are also different among the specimens. The particle sizes of SAP and the differences in the moisture distributions [20] could affect the initial evolution of internal friction. This may result in the differences in the subsequent expansive behaviors in mortars. Further study is needed to understand development of internal friction and its effect on movement of water at very early ages before the setting.

5.4 Conclusions

Influence of bleed water on early age volume changes in mortars with low water to cement ratios and expansive behavior of internally cured mortars with different SAPs are investigated. Major results obtained in this section are as follows;

- (1) The measurements of autogenous deformation can be influenced by bleeding before setting. As self-desiccation occurs, the bleed water may be reabsorbed to reduced

autogenous shrinkage, or even expansion. Reabsorption of bleed water may influence autogenous deformation for long term.

- (2) The reabsorption of the bleed water may accelerate the hydration of cement so that internal solid skeleton has formed earlier in the cementitious system, which results in the earlier expansion behavior and higher electrical resistivity.
- (3) A part of internal water is not consumed to compensate self-desiccation. Because the internal water is nonuniform distributed within the whole cement-based mixture, or the internal water cannot migrate from internal water reservoirs to the surrounding maturing cement paste and interact with cement pastes on the way successfully.
- (4) The incorporation of the viscosity enhancement agent can reduce the amount of free water in cement-based system. As a result, bleeding is reduced, and cement paste viscosity increases at very early age.
- (5) Early age expansion of the mortars with SAP is contributed from the internal water released from the SAP. The magnitude of the expansion and the extent of shrinkage reduction depend on the size of SAPs. The larger SAPs, the greater and the longer period of expansion. The absorption capacities of SAP are related to the transition periods of autogenous deformation from expansion to shrinkage. The smaller desorption rate, the longer expansion continued.
- (6) Even if the amounts of hydration products are almost the same, different expansive behaviors are seen in mortars with SAP. Expansive behavior of SAP mortars cannot be simply explained only by reabsorption of the internal bleed waters. Difference in expansive behavior of mortars with SAPs may be related to differences in the initial moisture distribution at the very early ages before the setting of cement.
- (7) When SAP is used as an internal curing material, the electrical resistivity begins to increase earlier than that in the control. The addition of SAP affects the development of the plastic viscosity.

REFERENCES

- [1] Mohr, B.J. and Hood, K.L.” Influence of bleed water reabsorption on cement paste autogenous deformation,” *Cement and Concrete Composites*, Vol. 40, No. 2, pp. 220-225, 2010.
- [2] Gaurav, S. et al.” The origin of early age expansions induced in cementitious materials containing shrinkage reducing admixtures,” *Cement and Concrete Research*, Vol. 41, No. 3, pp. 218-229, 2011.
- [3] Holt, E.” Contribution of mixture design to chemical and autogenous shrinkage of concrete at early ages,” *Cement and Concrete Research*, Vol. 35, Iss. 3, pp. 464-472, 2005.
- [4] Baroghel-B, V. et al.” Autogenous deformations of cement pastes, part II: W/C effects, micro-macro correlations, and threshold values,” *Cement and Concrete Research*, Vol. 36, No. 1, pp. 123-136, 2006.
- [5] Bjøntegaard, Ø., Hammer, T. A. and Sellevold, E. T.” On the measurement of free deformation of early age cement past and concrete,” *Cement and Concrete Composites*, Vol. 26, No. 5, pp. 427-435, 2004.
- [6] Cagnon, H. et al.” Effects of water and temperature variations on deformation of limestone aggregates, cement paste, mortar and High Performance Concrete (HPC),” *Cement and Concrete Composites*, Vol. 71, pp. 131-143, 2016.
- [7] Jensen, O.M. and Hansen, P.F.” Water-entrained cement-based materials: II. Experimental observations,” *Cement and Concrete Research*, Vol. 32, No. 6, pp. 973-978, 2002.
- [8] Igarashi, S. and Watanabe, A.” Experimental study on prevention of autogenous deformation by internal curing using super-absorbent polymer particles”, *Proceedings of the international RILEM conference, Denmark*, pp. 77-86, 2006.
- [9] Mechtcherine, V., Egor, S. and Christof, S.” Effect of superabsorbent polymers (SAPs) on rheological properties of fresh cement-based mortars-Development of yield stress and plastic viscosity over time,” *Cement and Concrete Research*, Vol. 67, pp.52-65, 2015.
- [10] Hasholt, M. T. And Jensen, O. M.” Chloride migration in concrete with superabsorbent polymers,” *Cement and Concrete Composites*, Vol. 55, pp. 290-297, 2015.
- [11] Sengul, O.” Use of electrical resistivity as an indicator for durability,” *Construction and Building Materials*, Vol. 73, No. 30, pp. 434-441, 2014.
- [12] Xiao, L.Z. and Li, Z.J.” Early-age hydration of fresh concrete monitored by non-contact electrical resistivity measurement,” *Cement and Concrete Research*, Vol. 38, No. 3, pp. 312-319, 2008.
- [13] Xiao, L.Z., Li, Z.J. and Wei, X.S.” Selection of superplasticizer in concrete mix design by

- measuring the early electrical resistivities of pastes,” *Cement and Concrete Composites*, Vol. 29, No. 5, pp. 350-356, 2007.
- [14] Sengul, O.,” Use of electrical resistivity as an indicator for durability,” *Construction and Building Materials*, Vol. 73, pp. 434-441, 2014.
- [15] Kamal, H. K.,” Viscosity-Enhancing Admixtures for Cement-Based Materials- An Overview,” *Cement and Concrete Composites*, Vol. 20, No. 2-3, pp. 171-188, 1998.
- [16] Igarashi, S., Aragane, N. and Koike, Y.,” Effects of spatial structure of superabsorbent polymer particles on autogenous shrinkage behavior of cement paste” *Proc. International RILEM Conference on Use of Superabsorbent Polymer and other new Additives in Concrete*, (Jensen, O.M., Hasholt, M.T. and Laustsen, S. eds.) RILEM S. A. R. L, Lyngby, Denmark, pp. 137-147, 2010.
- [17] Sant, G., Bentz, D. and Weiss, J.,” Capillary porosity depercolation in cement-based materials: Measurement techniques and factors which influence their interpretation,” *Cement and Concrete Research*, Vol.41, No. 8, pp. 854-964, 2011.
- [18] Mrzykowski, M. et al.,” Modeling of water migration during internal curing with superabsorbent polymers,” *Journal of materials in civil engineering*, Vol.24, No. 8, pp. 1006-1016, 2012.
- [19] Levita, G. et al.,”Electrical properties of fluidified Portland cement mixes in the early stage of hydration,” *Cement and Concrete Research*, Vol. 30, No. 6, pp.923-964, 2000.
- [20] Yokota, K. and Igarashi, S.,”Evaluation of clustered distribution of superabsorbent polymers and its relation to autogenous shrinkage behavior of internally cured mortars,” *Proc. 13rd International Conference on Durability of Building Materials and Components*, pp. 963-970, 2014.

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

6.1 Introduction

Due to high fluid absorption of SAP, it is useful to mitigate of autogenous shrinkage by internal curing [1, 2]. SAP has the feature to absorb water due to osmotic pressure, resulting in the formation of a swollen hydrogel [3]. On being introduced into the cementitious materials SAP takes up a part of mixing water, and this water will be released into the cementitious matrix for internal curing [4]. Therefore, additional water is added to compensate for the loss in workability of the mixture and to be used as entrained water [1, 2]. Some investigations were already made regarding the influence of SAP and the additional water on microstructural properties. Hasholt et al. [5] concluded that internal curing with SAP and additional water can mitigate autogenous deformation with a minimal loss of compressive strength, and the loss of compressive strength resulted from the increase in water to cement ratio of concrete with SAP and the additional water. It is also reported that a higher air pore content is observed in specimens with SAP and additional water [6]. The amount of additional water affects a relatively greater drying shrinkage [2]. Effect of internal curing water introduced by the pre-soaked SAP on shrinkage of high strength concrete has been investigated [7]. One of the conclusions is the reduction of relative humidity in concrete caused by cement hydration is significantly postponed with the addition of pre-soaked SAP. Besides autogenous deformation, effect of SAP and additional water on workability of the fresh concrete, mechanical properties and heat development during hydration are of interest.

Concerning the influence of additional water in workability of concrete, several researchers have studied the effects of simple addition of dry SAP without extra addition of water on the shrinkage and the mechanical properties of concrete. Just et al. [8] have reported that hydration is not stopped due to lack of free capillary pore but may instead continue thanks to the additional space introduced by the SAP without additional water. A less capillary porosity was observed in the cement pastes with SAP without additional water [9]. Without additional water, the total water to cement ratio is preserved. Furthermore the role of SAP in cementitious materials could keep functioning. Therefore, partial replacement of mixing water with SAP to form hydrogel formation is considered as a promising technique.

In this section, cement pastes and mortars with SAP are produced with additional water. This section focuses on effect of gelation of a part of mixing water with SAP on early age

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

properties of the cementitious materials. Comparison between the results of autogenous shrinkage, workability and mechanical properties at early age are discussed from the viewpoint of hydrogel formation due to SAP in different water contents.

6.2 Effect of partial gelation of mixing water with SAP on autogenous shrinkage behavior of cement paste with low water to cement ratio

6.2.1 Mixture proportion

Mixture proportion of cement pastes are given in Table 6-1. Cement pastes investigated in this section are already described in Sec. 3.1. A polycarboxylic acid type superplasticizer (SP) is added to the mix to control the flow. SAP-A and SAP-2 supplied from different manufacturers are used. Water to cement ratios of cement pastes are 0.28 and 0.33. Dosages of SAP-A and SAP-2 are determined to absorb 10% of mixing water. The amount of SAP-2L is also increased to absorb 20% of mixing water. In addition, for comparison, the cement paste with 0.39% SAP-2L to the mass of cement is produced to control the effective water to cement ratio to 0.28. Therefore, additional water is added to be absorbed by the SAP. The water absorbed by SAP and the effective water to cement ratio of the bulk cement matrix are also shown in Table 6-1.

Table 6-1 Mixture proportion of cement pastes (mass fraction)

Mixes	W/C	W _a /C	C	W _e	W _{SAP}	SAP	SP	Initial	Final	Flow
REF	0.28	0.28	1	0.280	-	-	0.0056	3:20	4:51	244
SAP-AL (10%W)	0.28	0.25	1	0.252	0.028	0.0028	0.0075	3:38	5:56	240
SAP-2L (10%W)	0.28	0.25	1	0.252	0.028	0.0022	0.0070	3:42	4:46	233
SAP-2S (10%W)	0.28	0.25	1	0.252	0.028	0.0022	0.0080	3:19	5:34	232
SAP-2L (20%W)	0.28	0.22	1	0.224	0.056	0.0042	0.0084	2:56	4:38	230
SAP-2L (0.39%C)	0.33	0.28	1	0.280	0.050	0.0039	0.0056	4:13	5:54	239

6.2.2 Results and discussion

(1) Autogenous deformation

Fig.6-1 shows autogenous deformation that is recorded immediately after casting. The REF mixture shows the largest deformation at 12 hours after casting to about 12 hours. After about 12 hours, the increase in shrinkage slows down and increases slightly. The mixtures with the SAPs exhibit a rapid increase in shrinkage until about the initial setting time, and then a slow expansion is observed until 6 hours. After 6 hours, shrinkage is observed in the mixtures with SAP, which is almost the same as the REF mixture. The addition of SAP greatly reduces subsequent shrinkage. The smallest shrinkage is observed for the mixture of SAP-2L (0.39%C) since its water to cement ratio is the greatest. Furthermore, the mixture with SAP-AL exhibits a larger shrinkage than that of the mixtures with SAP-2. When SAP-2 absorbing 10% of mixing water is included, the larger particle of SAP, the larger shrinkage is observed. The type and size of SAP affect the autogenous deformation. Besides, when SAP-2L absorbing 20% of mixing water is added, the mixture has a smaller shrinkage after the expansion than that of the mixtures of SAP-2L (10%W) and SAP-2S (10%W). The initial setting time is earlier for the mixture of SAP-2L (20%W) with the smallest the effective water to cement ratio (Table 6-1). The reduction effective water to cement ratio may affect microstructure of cement paste mixture at early age.

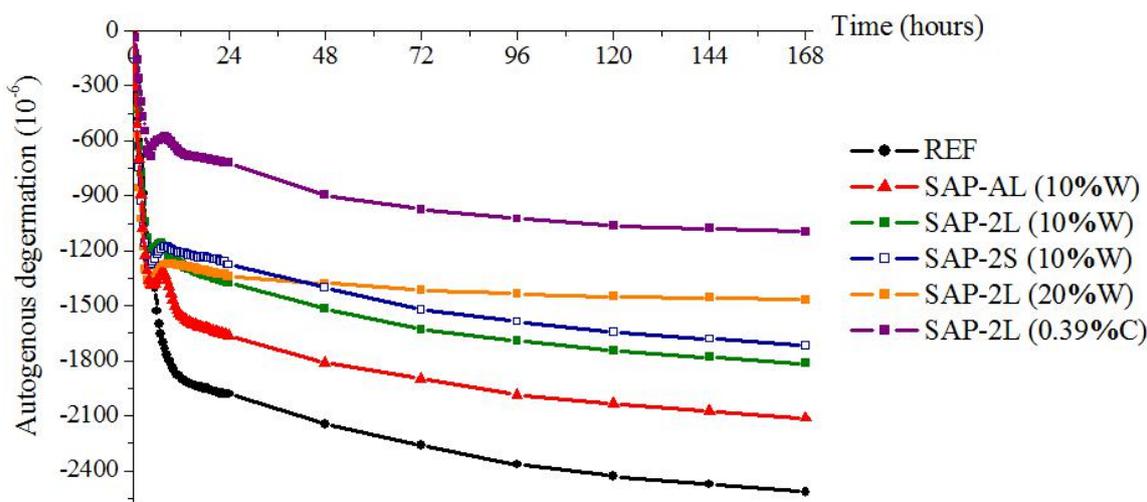


Fig.6-1 Autogenous deformation of cement pastes continuously recorded after casting

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

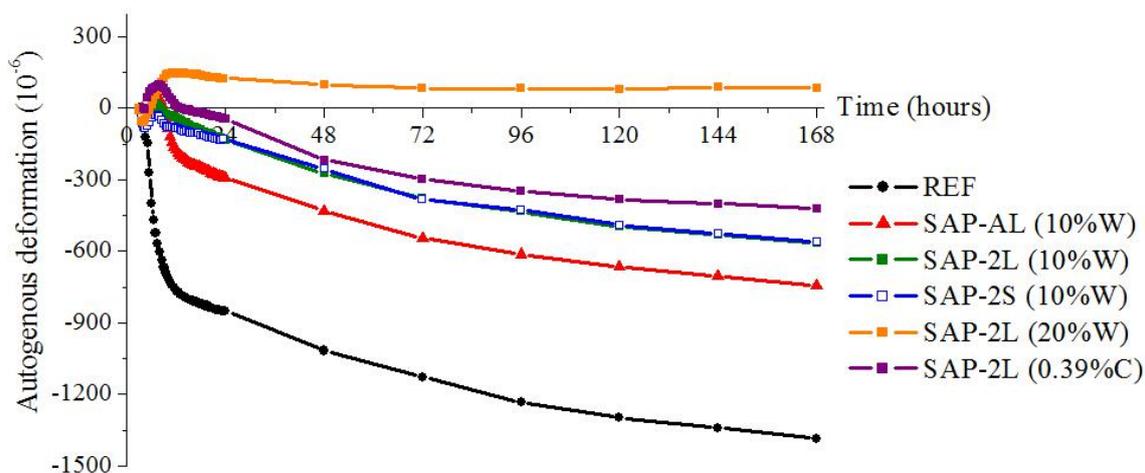


Fig.6-2 Autogenous deformation of cement pastes after the initial setting time

Fig.6-2 shows autogenous deformation after the initial setting time (i.e. deformation is adjusted to zero at the time of initial setting). The initial setting time is provided in Table 6-1. In the REF mixture, the trend of autogenous deformation is much similar to that in Fig.6-1, but the value is much smaller than that in Fig.6-1. However, it is still obviously found that the autogenous deformation is greater than that of the mixtures with SAP. The mixtures with SAP exhibit significant reduction in shrinkage than that in the REF mixture. In particular expansions observed for several hours after the time zero result in less shrinkage. The mixture with SAP-2L (20%W) has the greatest expansion and the smallest shrinkage, since the SAP absorbs the large amount of mixing water. It is found that the internal water released enough from SAP is effective to compensate for self-desiccation. Furthermore, the mixtures with SAP-AL (10%W), SAP-2L (10%W), SAP-2S (10%W) and SAP-2L (0.39%C) do not exhibit great differences in final shrinkage. In particular for the mixtures of SAP-2L (10%W), SAP-2S (10%W) and SAP-2L (0.39%C), their changes in autogenous shrinkage have a similar trend. In order to limit self-desiccation and autogenous shrinkage, additional water is added in the mixture with SAP-2L (0.39%C). This leads to the increase in the total water to cement ratio. For the mixture with SAP-AL (10%W), SAP-2L (10%W), and SAP-2S (10%W), 10% of mixing water is absorbed by SAP to form hydrogel, and the effective water to cement ratio is reduced. Therefore, internal gelation of mixing water with SAP can be used as an effective way to limit self-desiccation and autogenous shrinkage without adding more extra water, which may have an adverse effect in certain properties of the mixture.

Fig.6-3 shows the degree of hydration. The mixtures with SAP-2L (10%W) and SAP-2L (20%W) show a little greater the degree of hydration than that of the REF mixture at 6 hours, but the differences become relatively small at 24 hours. The mixture with SAP-2S (10%W) exhibits a similar degree of hydration to that of the REF mixture. The degree of hydration of the

Chapter 6 Effect of gelation of a part of mixing water with SAP
on early age properties of cementitious materials

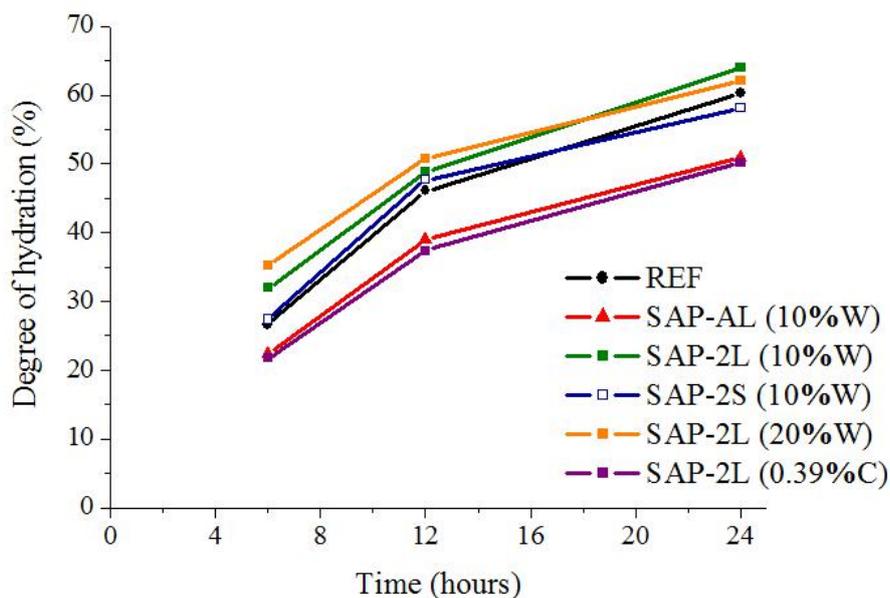


Fig.6-3 Changes in the degree of hydration of cement in cement pastes with SAPs

mixture with SAP-AL (10%W) is noticeably smaller than that of the REF mixture. Meanwhile, the degree of hydration of the mixture with SAP-2L (0.39%C) is the smallest during all the mixtures due to its greater total water to cement ratio.

Change in absorption capacity of SAP-A and SAP-2 in saturated solution of calcium hydroxide is provided in Fig.4-1 in Sec.4.2. It is showed here again to understand the relationships among the autogenous deformation, the degree of hydration and the absorption capacity of SAP. SAP-A absorbs the solution quickly and also desorpts solution quickly early in

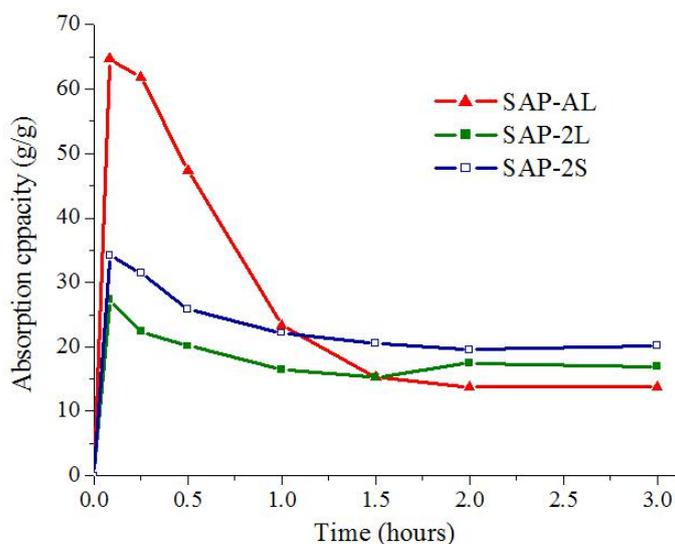


Fig.4-1 Change in absorption capacity in saturated solution of calcium hydroxide by the tea bag method

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

the dormant period, while the absorption capacity of SAP-2 decreases gradually. In other words, the internal curing water in SAP-2 can be kept longer to influence autogenous deformation for a long time. Christof et al. [10] have investigated that the appropriate time for SAP for optimum mitigation of autogenous shrinkage is not as early as the dormant period. SAP provides its water during the acceleration period and continues to desorb the water even in the deceleration period. This continuous release of internal water would affect mitigation autogenous shrinkage. Here, the mixture with SAP-AL (10%W) shows a relatively rapid increase in shrinkage after expansion may related with early and quickly release of internal water. Meanwhile, the lack internal water after the dormant period results to the greater value of shrinkage than that in the mixtures of SAP-2L (10%W) and SAP-2S (10%W) (Fig.6-2). Furthermore, the degree of hydration of the mixture with SAP-AL (10%W) is smaller than that of the mixtures with SAP-2L (10%W) and SAP-2S (10%W) after the dormant period (Fig.6-3). Hence, the good performance of SAP-2 in mitigating autogenous shrinkage and accelerating the hydration of cement are obviously a direct result of proper release of water.

(2) Measurements of electrical resistivities and compressive strength

The electrical resistivities of mixtures are shown in Fig.6-4. All the mixtures exhibit similar tendencies in electrical resistivity with time. The times when the resistivity begins to increase are almost the same, regardless of SAP addition. The electrical resistivity of the REF mixture increases rapidly from 2 hours to about the final setting time, then increases gradually. The similar tendencies to the REF mixture are observed in the mixtures with SAP-AL (10%W), SAP-2L (10%W) and SAP-2S (10%W), while their resistivities are slightly greater than the

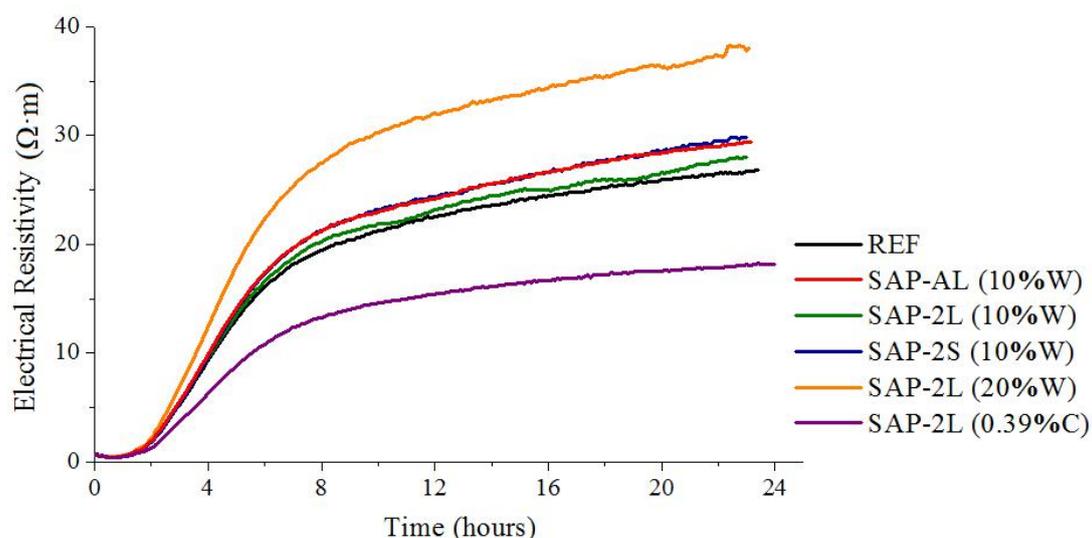


Fig.6-4 Development of electrical resistivity in cement pastes with SAPs

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

REF mixture. It is noticed that the electrical resistivity in the mixture with SAP-2L (20%W) shows a rapid increases and reaches a greater value than the REF mixture and the mixtures with SAP-2L (10%W) and SAP-2S (10%W), even if their degrees of hydration are not quite different (Fig.6-3). Here, since the four kinds of mixtures have the same total water to cement ratio and similar degree of hydration, effect of pore solution composition on electrical resistivity can be ignored. On the other hands, the electrical resistivities at 24 hours are consistent with the effective water to cement ratio, which is adjusted by the SAP. The smaller the effective water to cement ratio, the greater the final electrical resistivity. In other words, when SAPs are added to absorb different amount of mixing water, the pore structure and pore connectivity of cement paste structure are changed. Furthermore, the mixture with SAP-2L (0.39%C) exhibit the smallest electrical resistivity. Therefore, the mixtures containing partial gelation of mixing water with SAP are easier to reduce the porosity, and produce the internal solid skeleton earlier. This promotes the development of electrical resistivity. However, when an extra water is added to the mixture, it introduces new pores in cement paste matrix. This increases connectivity of capillary pore networks. As a result, more porous structure are formed in the cement matrix.

Fig.6-5 shows compressive strength at 7 days. All the mixtures with SAP have smaller compressive strength than the REF mixture. Although the degrees of hydration for the mixtures with SAP-2L (10%W) and SAP-2L (20%W) are a little larger than that of the REF mixture (Fig.6-3), the addition of SAP-L always reduces compressive strength. The additional voids created by SAP are the reason for compressive strength reduction. The increase in the degree of hydration could increase strength, however it cannot compensate the reduction in strength due to the addition of SAP [11]. The mixture with SAP-2L (0.39%C) exhibits a lower compressive strength than the other mixtures. In the mixture with SAP-2L (0.39%C), even if the degree of hydration is almost the same as that of the mixture with SAP-AL (10%W) (Fig.6-3), the decrease in compressive strength is greater. Furthermore, in the mixtures with SAP-2L (10%W),

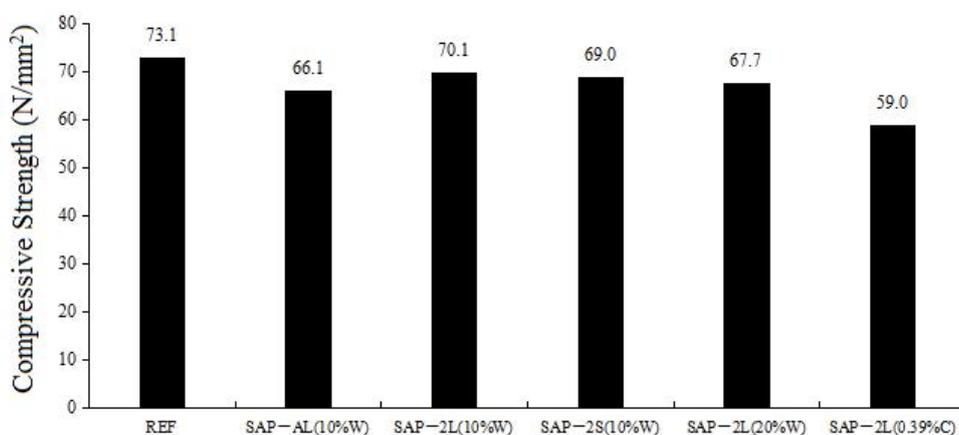


Fig.5-5 Compressive Strength of cement pastes with SAPs at 7days

SAP-2S (10%W) and SAP-2L (0.39%C), their effect on the migration of the autogenous deformations zeroed at the initial setting is almost with the same extent (Fig.6-2). However, their effects on the compressive strength is obviously different. Therefore, when SAP is used by the two different ways, the compressive strength at 7 day is reduced to different degrees. However, it should be noted that internal gelation of a part of mixing water with SAP results in less decrease in compressive strength. Therefore, internal gelation of a part of mixing water with SAP seems a promising way for mitigation of autogenous shrinkage.

(3) Spatial structure of capillary pores

Fig.6-5 shows two-point cluster function of capillary pores at 24 hours. The function for the mixture with SAP-2L (0.39%C) shows the greatest in the mixtures, as well as the initial value of the function. There is little difference between the functions of the mixtures with SAP-2L (10%W) and SAP-2L (20%W). The initial value of two-point function is determined by the porosity [12]. Therefore, there must be different in the porosity between the mixtures with two different ways for SAP addition. The porosity in the mixture with SAP-2L (0.39%C) is greater due to the greater initial value of the function, which may result in the small electrical resistivity (Fig.6-4). Furthermore, the distances that the functions decay to the horizontal axis are shown in Fig.6-5. The distance that the function of the mixture with SAP-2L (0.39%C) decays to the horizontal axis is about 20 μ m, while it is about 12 μ m in the functions of the mixture with SAP-2L (10%W) and SAP-2L (20%W). If the length at which the function converges on the abscissa is defined as the maximum length, this length can be related to the maximum size of pores [12]. The maximum size of visible capillary pores in the mixture with

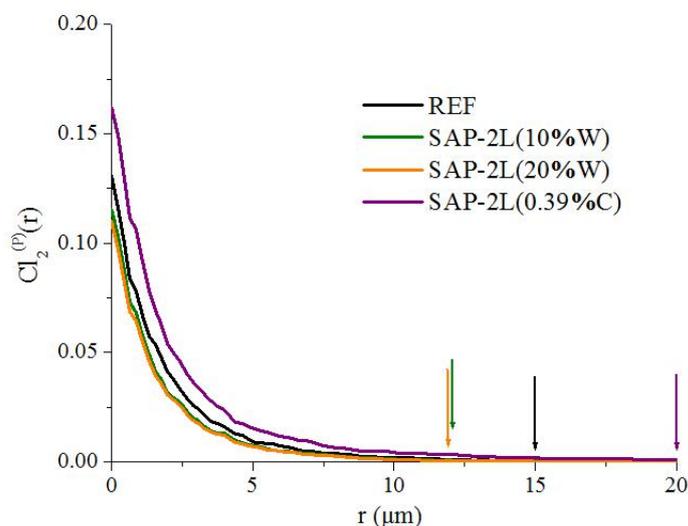


Fig.6-6 Two-point cluster function of capillary pore in cement pastes with SAP-2L

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

SAP-2L (0.39%C) is larger than that in other mixtures. Taking account of the coarse capillary pores in the mixture with SAP-2L (0.39%C), formation of capillary pore networks in the mixture may be a little delayed. As a result, the internal water from SAP can travel into surrounding mature cement paste, and interact with the cement paste for a little longer time than that in the mixture with SAP-2L (10%W) and SAP-2L (20%W). This may lead to the slight greater in autogenous shrinkage reduction (Fig.6-2). However, the influence is quite small on the whole. Therefore, gelation of a part of mixing water with SAP still can be used as effective way to mitigate autogenous shrinkage and keep high performance of cement-based materials.

6.3 Effect of gelation of mixing water with SAP on early age properties of mortars with high water to cement ratios

6.3.1 Mixture proportion

Mixture proportion of mortars is given in Table 6-2. Cement paste investigated in this section is already described in Sec. 3.1. The fine aggregate used here is river sand. SAP-D and SAP-3 that are produced by the different methods are used. Water to cement ratios of cement paste are 0.55 and 0.58. Dosages of SAP-D and SAP-3 are determined to absorb 5% of mixing water. The amount of SAP-D is also increased to absorb 10% of mixing water. In addition, dosages of SAP-D and SAP-3 are also determined about 0.1% and 0.2% by the cement weight, respectively. To control the effective water to cement ratio to 0.55, extra water is necessary for SAP to absorb. The water absorbed by SAP and the effective water to cement ratio of the bulk cement matrix is also shown in Table 6-2.

Table 6-2 Mixture proportion of cement pastes (mass fraction)

Mixes	W/C	W _e /C	C	S	W _e	W _{SAP}	SAP	Initial	Final	Flow
REF	0.55	0.55	1	2	0.55	-	-	5:30	6:49	214
SAP-D (0.1%C)	0.58	0.55	1	2	0.55	0.03	0.001071	5:34	7:23	220
SAP-D (5%W)	0.55	0.52	1	2	0.52	0.03	0.001071	5:27	6:50	200
SAP-D (10%W)	0.55	0.50	1	2	0.50	0.055	0.002143	5:34	6:50	181
SAP-3 (0.2%C)	0.58	0.55	1	2	0.55	0.03	0.002256	5:36	7:25	200
SAP-3 (5%W)	0.55	0.52	1	2	0.52	0.03	0.002256	5:40	6:46	196

6.3.2 Results and discussion

(1) Measurements of volume change of mortars with SAP

The flow values are provided in Table 6-2. It should be noted that the flows of the mortars with SAP-D (5%W), SAP-D (10%W) and SAP-3 (5%W) are smaller than others. In other words, gelation of a part of mixing water with SAP reduces the flow, due to the reduction of free water. The initial setting time is also provided in Table 6-2. There is little difference between the initial setting times of mortars, while, the final setting times of the mortars with SAP-D (0.1%C) and SAP-3 (0.2%C) are about half an hour later than the others. Therefore, gelation of extra water with SAP slightly postpones the final setting.

Fig.6-7 shows autogenous deformation after the initial setting time (i.e. deformation is adjusted to zero at the time of initial setting). There is obviously change in the REF mortar after the initial setting to 1 day. After 1 day, the autogenous deformation due to shrinkage develops slowly. In contrast to the REF mortars, the mortars with SAP exhibit expansion after the initial setting. The mortars that contain water gelled with SAP exhibit expansion. The systems of mortars with extra water for SAP hydrogel shrink continuously after the initial expansion, and the final shrinkage is smaller than the REF mortar. The mortars without extra water for SAP hydrogel kept their expansions by 7 days. Furthermore, the mortar with SAP-D (10%W) exhibits the greatest expansion, in which SAP absorbs most amount of the mixing water. It is clearly found that the early age expansion is related to the internal water conditions of gelation with SAP and the amount of internal water from SAP. The replacement of mixing water with

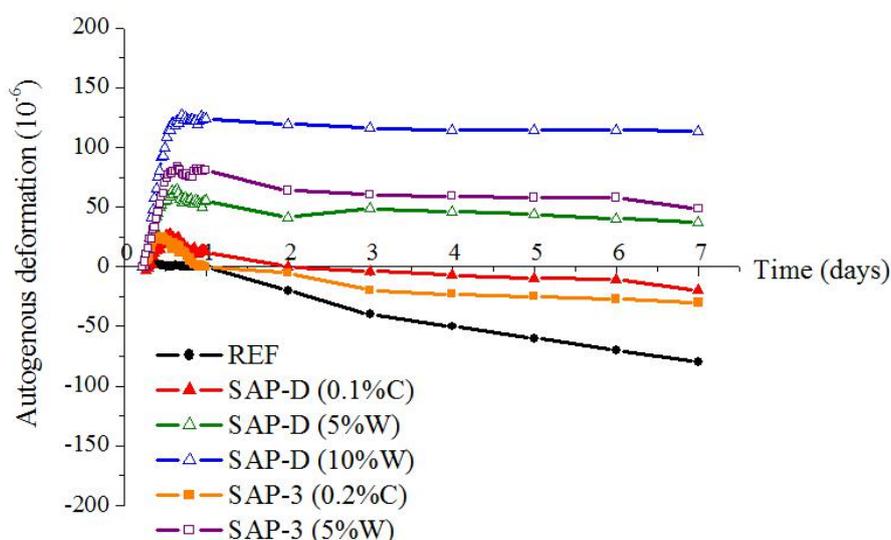


Fig.6-7 Autogenous deformation of mortars with SAP

Chapter 6 Effect of gelation of a part of mixing water with SAP
on early age properties of cementitious materials

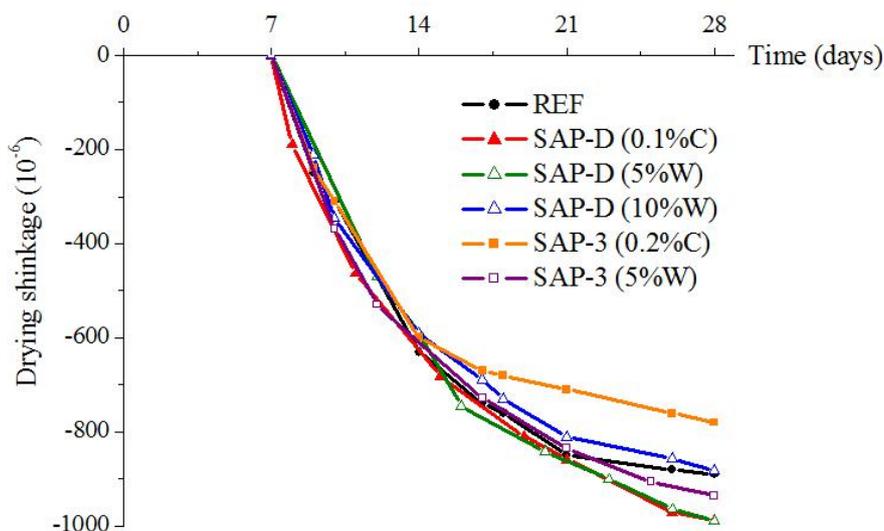


Fig.6-8 Drying shrinkage of mortars with SAP measured after 7 days

gelled SAP is more effective than the gelation of extra water with SAP in reduction in shrinkage, even if their amounts of gelation is almost same. The more mixing water SAP absorbed, the larger initial expansion observed. The reduction in autogenous shrinkage results from the initial expansion.

Fig.6-8 shows the drying shrinkage of mortars measured after 7 days. All of the mortars shrink rapidly from 7 days to about 14 days, then shrinkage develops slowly than before. The mortar with SAP-3 (0.2%C) exhibits the smallest drying shrinkage, while there is little difference between the drying shrinkage among the other mortars.

Combining the autogenous shrinkage (Fig.6-7) and the drying shrinkage (Fig.6-8), the total volume change of mortars is given in Fig.6-9. The autogenous shrinkage of the REF mortar develops slowly after 1 day to 7days, while as soon as cured in the dry condition, a rapid shrinkage is observed. The mortar with SAP-D (0.1%C) exhibits a reduction in autogenous shrinkage than the REF mortar (Fig.6-7), while its effects on drying shrinkage is not obviously (Fig.6-8). On the contrary, the mortar with SAP-3 (0.2%C) exhibits a significantly reduction in drying shrinkage. As a result, the total volume change at 28 day of the mortar with SAP-3 (0.2%C) is smaller than that of the mortar with SAP-D (0.1%C). Furthermore, the mortar of SAP-D (10%W) exhibits a smallest volume change at 28 day than that of the mortars with SAP-D (5%W) and SAP-3 (5%W). Effect of the mortar with SAP-D (10%W) on autogenous shrinkage reduction displays remarkable than others, due to its greatest initial expansion. As a result, the smallest volume change is observed. Therefore, the reduction in total volume change with SAP results from the reduction in autogenous shrinkage. Gelation of a part of mixing water with SAP has reduced autogenous shrinkage considerably whereas drying shrinkage is less

Chapter 6 Effect of gelation of a part of mixing water with SAP
on early age properties of cementitious materials

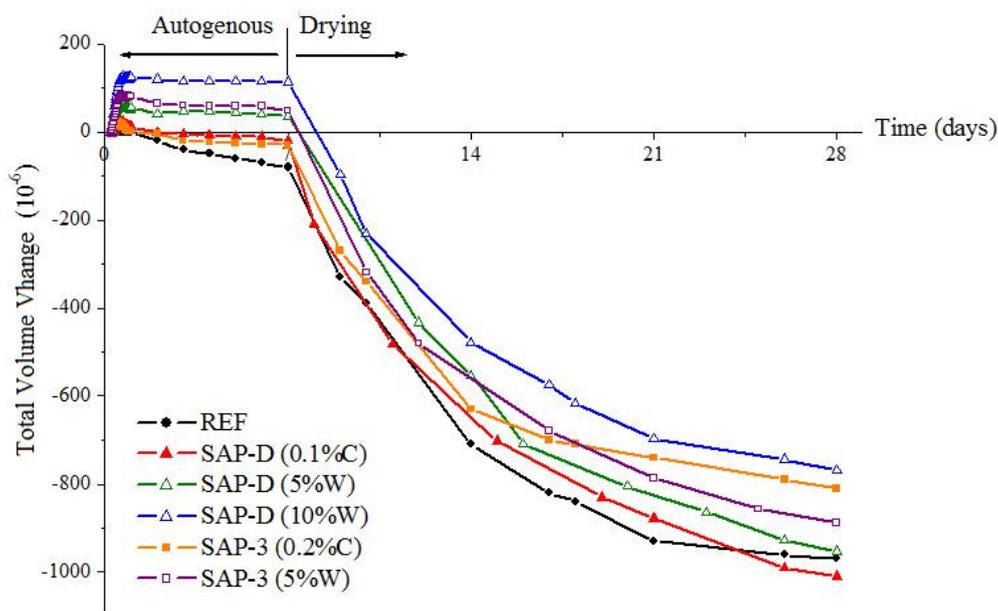


Fig.6-9 Total volume change of mortars with SAP

reduced.

The mass loss in mortars during drying curing is presented in Fig.6-10. The mass losses of all mortars increase steeply in the first 14 day. Then the mass losses increase gently. The mass losses of mortars containing hydrogel of SAP are less than the REF mortar. The mass loss of the mortar with SAP-D (10%W) is smaller than that of the mortars with SAP-D (5%W) and SAP-3 (5%W). It indicates that the increase of mass loss depends on SAP content. The free water in mortars is reduced due to absorption of SAP. The more SAP is added, the little free water is present in the mortars. In the case that extra water is added in mortar for gelation, the extra

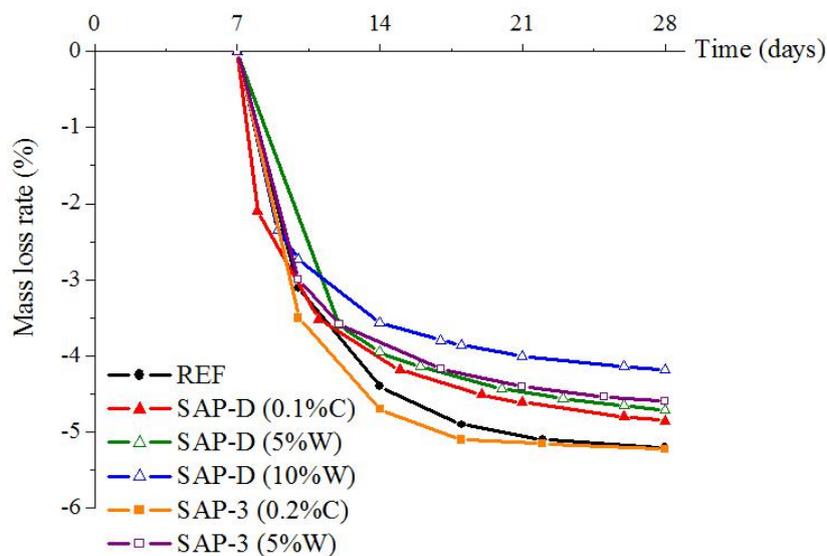


Fig.6-10 Mass loss rate for mortars with SAP

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

water results in the greater mass loss than the mortar in which no extra water is added for SAP. Furthermore, although the total water to cement ratios of the mortars with SAP-D (0.1%C) and SAP-3 (0.2%C) are greater than the REF mortar, the mortars with SAP-D (0.1%C) and SAP-3 (0.2%C) do not have greater mass loss than the REF mortar. The form of the additional water is not conventional free water. It has become hydrogel, and been distributed randomly in cement paste mixture. The mixing of free water and hydrogel in cement-based systems may affect the potential water loss. In addition, the relationship between mass losses and drying shrinkage at 28 days is not distinct. The contribution of the lost water to drying shrinkage is small due to the less content of water loss.

(2) Early age properties of mortars with SAP

The degree of hydration is shown in Fig.6-11. At 6 hours, there are little differences in the degree of hydration between the mortars. The degrees of hydration in the REF mortar and the mortars with SAP-D (5%W) and SAP-D (10%W) are relative higher than other mortars at 12 hours. However, differences in the degree of hydration between the mortars are relatively small at 24 hours. In the other words, at 24 hours after water addition, the internal RH still keeps high, and the amount of hydration productions could be considered as the same. However, the autogenous shrinkage especially expansion in the SAP mortars develops to different degrees at that time (Fig.6-7). Therefore, effect of early age hydration on volume change in mortars with SAP is small. The state of free water is changed by partial replacement of mixing water with hydrogel, or the extra water for SAP. Hydrogel of SAP could affect the initial volume change at early age (Fig.6-7). This may result in the differences in the subsequent autogenous shrinkage

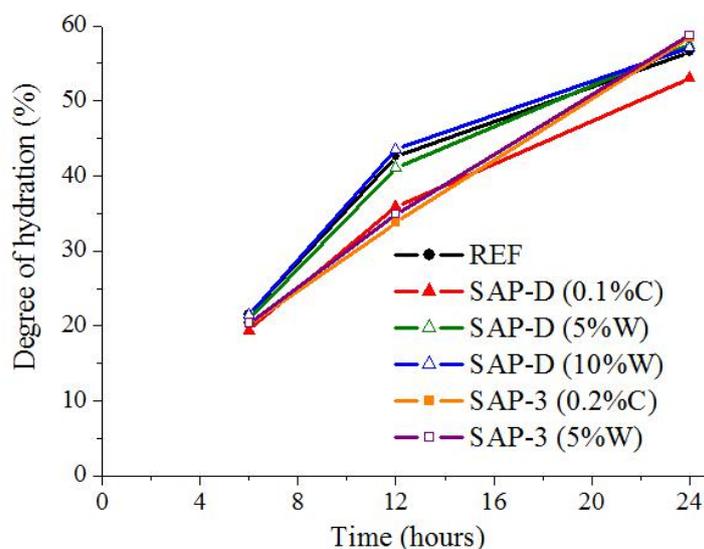


Fig.6-11 Changes in the degree of hydration of cement in mortars with SAPs

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

behaviors in mortars.

Changes in resistivity with time are shown in Fig.6-12. All the mortars exhibit a similar tendency in electrical resistivity. The electrical resistivity slowly decreases at first and then gradually increases with time. When SAP-3 is used, the electrical resistivity is slightly smaller than that of the REF mortar. In particular, the mortar with SAP-3 (0.2%C) exhibits a significant lowest electrical resistivity. Effect of the hydration of cement on the electrical resistivity could be almost the same since all the mortars have the same degree of hydration (Fig.6-11). The pore solution composition and pore connectivity are the major factors to dominate the electrical resistivity. Effects of the pore solution conductivity on the electrical resistivity are also the same in the REF mortar and the mortar with SAP-3 (0.2%C) since their total water to cement ratio is the same. Therefore, there must be some difference in pore connectivity in the mortar with SAP-3 (0.2%C). The connectivity of capillary pore networks in the mortar with SAP-3 (0.2%C) might be better than those of the other mortars, taking account of the smallest electrical resistivity. When extra water is add to the mortar, the additional water produces more capillary pores in the mortars. As a result, a better connectivity of capillary pore networks is attained. The internal water condition of the mortar with SAP-D (0.1%C) is the same as the mortar with SAP-3 (0.2%C). However, their electrical resistivities are quite different. It may be related to the size of SAP particles. The voids created by SAP-D in cement-based material system is smaller than that of the mortars with SAP-3, since the particle size of SAP-D is much smaller than SAP-3. Therefore, narrow networks of capillary pore are formed in the cement matrix with SAP-D. The narrow networks of capillary pore lead to the greater electric resistivity.

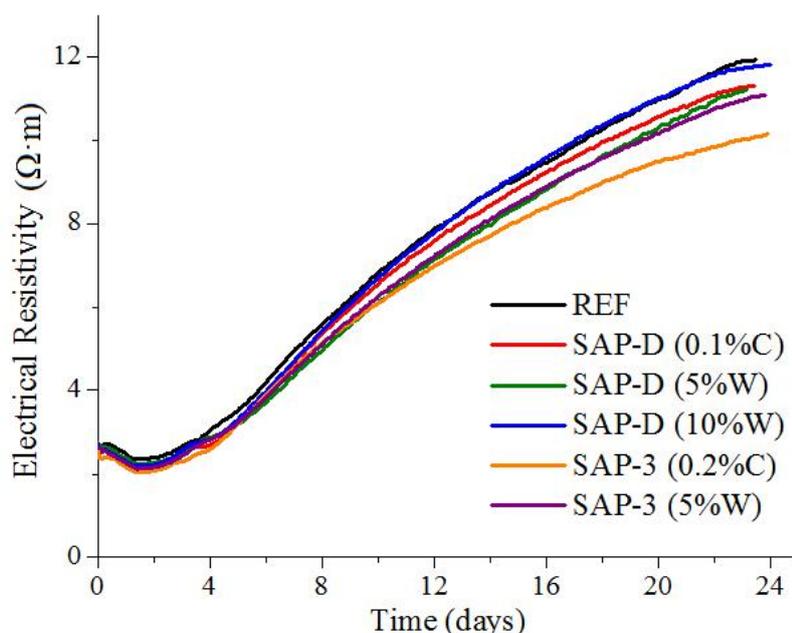


Fig.6-12 The electrical resistivity of mortars with SAPs

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

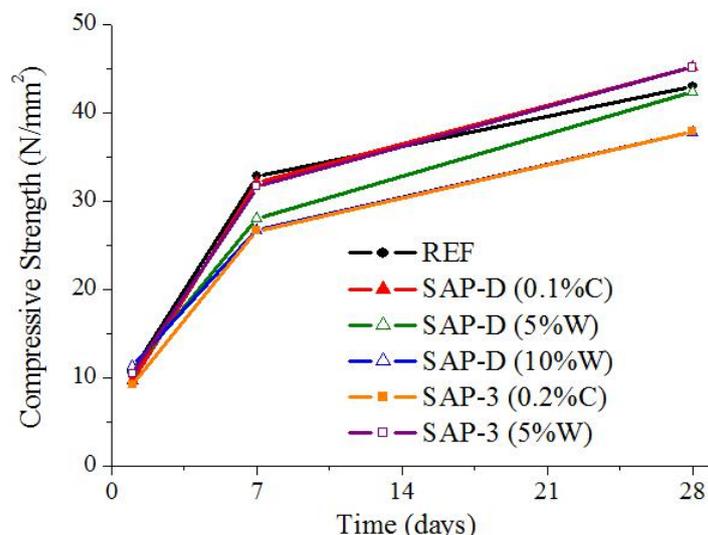


Fig.6-13 Compressive Strength in mortars with SAPs measured at 7days

Compressive strength is shown in Fig.6-13. In the case of the mortars with extra water addition, the compressive strength of the mortars with SAP-D (0.1%C) and SAP-3 (0.2%C) are consistent with their electrical resistivity (Fig.6-12). The compressive strength of the mortar with SAP-D (0.1%C) is very close to the value of the REF mortar, while the value of the mortar with SAP-3 (0.2%C) is obviously smaller. The reduction of the compressive strength may be related to the capillary pore structure which is influenced by the size of SAP particle as mentioned above. Meanwhile, in the case of the mortars which a part of mixing water is gelled with SAP, the compressive strength of the mortars with SAP-D (5%W) and SAP-3 (5%W) is almost the same as that of the REF mortar. The voids created by SAP may be filled with the hydration products during hydration process. Therefore, effect of SAP on compressive strength reduction is not distinct. However, the compressive strength of the mortars with SAP-D (10%W) is obviously smaller. Amount of the hydration produce could be almost the same among the mortars with SAP-D (5%W), SAP-3 (5%W) and SAP-D (10%W) due to the same degrees of hydration (Fig.6-11). The hydration produce could not completely fill the voids in the system of the mortars with SAP-D (10%W). As a result, a smaller compressive strength is observed. On the other hands, there is little different between the compressive strength of the mortars with SAP-D (10%W) and SAP-3 (0.2%C), even if the amount of hydrogel are different between them. Therefore, it cannot simply concluded that the lower compressive strength is a result of amounts of hydrogel with SAP. The way that a part of mixing water gelled with SAP shows less impact on compressive strength, even with amounts of hydrogel.

Chapter 6 Effect of gelation of a part of mixing water with SAP on early age properties of cementitious materials

6.4 Conclusions

Effect of gelation of a part of mixing water with SAP on early age properties of mortars are investigated. Major results obtained in this section are as follows;

- (1) All mortars with SAP exhibit expansion. Mitigation of autogenous shrinkage with SAP results from the initial expansion.
- (2) Gelation of a part of mixing water with SAP can be used as effective way to mitigate self-desiccation and autogenous shrinkage without adding extra water. The good performance of SAP in mitigating autogenous shrinkage and accelerating hydration is obviously results from release of the absorbed water after the dormant period.
- (3) The reduction in total volume change with SAP results from the reduction in autogenous shrinkage. Gelation of a part of mixing water with SAP has reduced autogenous shrinkage considerably whereas drying shrinkage is less reduced.
- (4) The hydrogel of SAP is easier to reduce the porosity, and produce the internal solid skeleton earlier. This promotes the development of electrical resistivity. While the extra water for SAP introduces new pores in cement paste matrix. This increases connectivity of capillary pore networks. As a result, more porous structure are formed. Smaller particle size of SAP leads to a greater electric resistivity, due to the formation of narrow networks of capillary pore in the cement matrix.
- (5) Gelation of a part of mixing water with SAP results in less decrease in compressive strength in mortars with low water to cement ratio. Effect of SAP on compressive strength reduction in mortars with high water to cement ration is not distinct. Since the voids created by SAP may be filled with the hydration products during hydration process. The way that a part of mixing water gelled with SAP shows less impact on compressive strength, even the amount of hydrogel is more than that SAP hydrogel with extra water.

Chapter 6 Effect of gelation of a part of mixing water with SAP
on early age properties of cementitious materials

REFERENCES

- [1] Jensen, O.M. and Hansen, P.F.,” Water-entrained cement-based materials I. Principles and theoretical background,” *Cement and Concrete Research*, Vol. 31, No. 4, pp. 647-654, 2001.
- [2] Jensen, O.M. and Hansen, P.F.,” Water-entrained cement-based materials: II. Experimental observations,” *Cement and Concrete Research*, Vol. 32, No. 6, pp. 973-978, 2002.
- [3] Zhu, Q. et al.” Effect of ionic crosslinking on the swelling and mechanical response of model superabsorbent polymer hydrogels for internally cured concrete,” *Materials and Structures*, Vol.48, No.7, pp.2261-2276, 2015.
- [4] Snoeck, D. et al.” The effect of superabsorbent polymers on the microstructure of cementitious materials studied by means of sorption experiments,” *Cement and Concrete Research*, Vol. 77, pp. 26-35, 2015.
- [5] Hasholt, T. H. et al.” Can superabsorbent polymers mitigate autogenous shrinkage of internally cured concrete without compromising the strength?,” *Construction and Building Materials*, Vol.31, pp.226-230, 2012.
- [6] Mönnig, S. and Lura, P.” Superabsorbent polymers-An additive to increase the freeze-thaw resistance of high strength concrete,” *Advances in construction material*, Springer Berlin Heidelberg, pp.351-358, 2007.
- [7] Kong, X., Zhang, Z. and Lu, Z.” Effect of pre-soaked superabsorbent polymer on shrinkage of high-strength concrete,” *Materials and Structures*, Vol.48, No.9, pp.2741-2758, 2015.
- [8] Justs, J. et al.” Internal curing by superabsorbent polymers in ultra-high performance concrete,” *Cement and Concrete Research*, Vol.76, pp.82-90, 2015.
- [9] Igarashi, S. and Watanabe, A.” Experimental study on prevention of autogenous deformation by internal curing using super-absorbent polymer particles,” *Proceedings of the international RILEM conference*, Denmark, pp. 77-86, 2006.
- [10] Schroefl, C. et al.” Sorption kinetics of superabsorbent polymers (SAPs) in fresh portland cement-based pastes visualized and quantified by neutron radiography and correlated to the progress of cement hydration,” *Cement and Concrete Research*, Vol.75, pp.1-13, 2015.
- [11] Hasholt, T. H., Jespersen, M. H. S. And Jensen, O.M.” Mechanical properties of concrete with SAP part I: Development of compressive strength,” *Proc. International RILEM Conference on Use of Superabsorbent Polymer and other new Additives in Concrete*, (Jensen, O.M., Hasholt, M.T. and Laustsen, S. eds.) RILEM S. A. R. L, Lyngby, Denmark, pp.117-126, 2010.

Chapter 6 Effect of gelation of a part of mixing water with SAP
on early age properties of cementitious materials

- [12] Igarashi, S., Wakanabe, A. And Kawamura, M.” Evaluation of capillary pore size characteristics in high-strength concrete at early ages,” Cement and Concrete Research, Vol.35, pp.513-519, 2005.

Chapter 7 Conclusions

Absorption and desorption behaviors of SAP and their effects on volume changes in cement-based materials are experimentally investigated. As far as this study is concerned, main conclusions can be summarized as followed;

In Chapter 1, the background and scope of this study are presented. Mechanisms of early age volume changes of concrete and internal curing, which are the bases of this study, are briefly reviewed.

In Chapter 2, theoretical background about absorption and desorption mechanism of SAP is discussed with relevant results in the literature. As a promising and multifunctional admixture, SAP has been of great interest. More recently, RILEM has established a Technical Committee, RILEM TC 260-RSC “Recommendations for Use of superabsorbent Polymers in Concrete Construction” (Chair: Prof. V. Mechtcherine, TU Dresden) to study a simple pre-test on SAP to disclose fundamental properties towards application in cement-based construction materials. Their reach activity is taken into account to make a research plan of this study.

Chapter 3 introduces materials and experiments in this study. Here, taking account of the current activity RILEM TC 260-RSC, cement slurry filtrate is recommend as a promising solution for assessing a qualitative estimate of the absorption capacity of SAP.

In Chapter 4, effects of various alkaline solution on the absorption and desorption behavior of different SAPs are investigated by three different method. Rheological behaviors of SAP mixtures are discussed in relation to the absorption capacity of SAP. It is suggested that the results of the modified tea bag method is easier to be affected by agglomeration of SAP particles, which seems to lead to insufficient swollen SAP. The increase in absorption capacity during the test period in the tea bag method is contributed by the retention of interparticle liquid. The graduate cylinder method is considered as a useful way to evaluate absorption capacity in cement environment. 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. The addition of SAP also affects the development of the plastic viscosity since it changes the amount of freely available water to alleviate internal friction. The particle sizes of SAP and their initial distribution could affect the initial evolution of internal friction.

Chapter 5 discusses the effects of reabsorption of bleed water and SAP addition on the autogenous deformation behaviors in relation to the initial expansion. The measurements of autogenous deformation is influenced by bleeding before setting. As self-desiccation occurs, the bleed water may be reabsorbed to reduce autogenous shrinkage, or even expansion. Reabsorption of bleed water also influences autogenous deformation for long term. A part of

Chapter 7 Conclusions

internal water is not consumed to compensate self-desiccation. This is because the internal water is not uniformly distributed within the whole cement-based mixture, or the internal water cannot migrate well. Early age expansion of the mortars with SAP is contributed from the internal water released from the SAP. The magnitude of the expansion and the extent of shrinkage reduction depend on the size of SAPs. The larger SAPs, the greater and the longer period of expansion. Difference in expansive behavior of mortars with SAPs may be related to differences in the initial moisture distribution at the very early ages before the setting of cement.

In Chapter 6, relationships among autogenous shrinkage, workability and mechanical properties are discussed from the viewpoint of hydrogel formation due to SAP addition at different water contents. Gelation of a part of mixing water with SAP can be used as an effective way to mitigate self-desiccation and autogenous shrinkage without adding extra water whereas drying shrinkage is less reduced. The reduction in total volume change with SAP results from the reduction in autogenous shrinkage. The good performance of SAP in mitigating autogenous shrinkage and accelerating hydration obviously result from release of the absorbed water after the dormant period. The hydrogel of SAP is easier to reduce the porosity, and produce the internal solid skeleton earlier. This promotes the development of electrical resistivity. Gelation of a part of mixing water with SAP results in less decrease in compressive strength in mortars. Effect of SAP on compressive strength reduction in mortars with high water to cement ration is not distinct. The way that a part of mixing water gelled with SAP shows less impact on compressive strength, even the amount of hydrogel is more than that of SAP hydrogel with extra water.

For promoting the application of SAP in construction industry, there are many aspects of SAP that should be understood. Further study is necessary with regard to the following issues.

- (1) In this study, SAP produced by aqueous polymerization and inverse suspension polymerization are used. Their differences in absorption and desorption behaviors has been investigated in Chapter 4. This two kinds of SAP have been widely used under laboratory conditions by many researchers. However, the most promising SAP in terms of its particle application is not fully understood. SAP is an organic material, and it is possible to design a new kind of SAP with the optimum properties such as shape, particles size and absorption capacity in accordance with the application in construction industry.
- (2) Three methods are used for investigating absorption capacity of SAP. However, practical and simple tests on absorption capacity of SAP have not been standardized yet. A standard method should be developed to disclose fundamental properties towards application in actual cementitious environments. RILEM TC 260-RSC is working in this direction. According to the results of this study, capillary forces between SAP particles, agglomeration of SAP particles and visibility of absorption and desorption processes should be taken into

Chapter 7 Conclusions

account in determining the measuring procedure in details.

- (3) This study indirectly estimates the distribution of SAP particle and water migration in cement-based materials by observing the changes in rheological properties, the degree of hydrations, or the electrical resistivities since it is difficult to determine within cement-based materials. Taking account of using SAP instead of air entertainment for providing frost resistance, it is important to evaluate the distribution with regard to spacing between SAP particles. Therefore, further research is necessary to reveal the real distribution of SAP.
- (4) As mentioned repeatedly in this study, SAP is a relatively new materials as an additives in concrete. Intensive research works are in progress in the world, especially in European countries. RILEM has formed a technical committee to work on the application of SAP in concrete. The specified technical committee is aiming at establishing the recommendations for the use of SAP to the practitioners. There is no doubt that SAP could be an effective admixture for future concrete. However, there have been only a few studies in Japan. Hope SAP could get more and more attention in Japan, even in other Asian countries.

Acknowledgments

Acknowledgments

Finally, it is the last part of this thesis. Here I would like to express my thanks and appreciation to all of those for being part of the journey of this three years and making possible of this thesis.

I would like to express my deepest gratitude to my supervisor Prof. Dr. Igarashi, you have been a tremendous mentor for me. Without your enthusiasm, encouragement and support, this thesis would hardly have been complete. Your advice on both research as well as my career have been priceless. I would also like to thank my assistant teacher Mr. Yamado for supporting my research. I would like to thank the members of laboratory of Prof. Igarashi: Mr. Yamazaki, Ms. Yamada, Mr. Okakura, Mr. Murotani, Ms. Wang Wen and Mr. Tिकासou. All of you have been there to support me during every stage of my time in laboratory. Especially I want to express my gratitude to Mr. Yamazaki for working together with me over the past two and a half years until your graduation.

My deep and sincere gratitude to my family for their continuous and unparalleled love, help and support. I am forever indebted to my parents for giving me the opportunities and experiences that have made me who I am. I am grateful to my sister for always being my side as a friend. I am grateful to my husband who is always there for me, no matter the best and the worst, the difficult and the easy. Thank to my dearest son, who make my life meaningful and make me much happier.

A very special gratitude to The China Scholarship Council (CSC) for providing the funding for my Ph.D study in Japan. The great motherland is always the strongest supporter for overseas students.

Last but not lest, I would like to shear my favorite quotation from the book *Damage to Concrete Structure* as the ending: Human life is more complex than concrete.