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Basics of analytical methods used for the investigation of interaction mechanism between cements and superplasticizers

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ABSTRACT

In order to better understand the interactions between cements and superplasticizers (high-range water reducers), various analytical methods have traditionally been applied, but some of these methods can introduce significant errors. In this paper the fundamental interaction mechanisms are reviewed and appropriate methods and sample preparation conditions are explained in detail. For superplasticizer adsorption measurements, analysis by size exclusion chromatography is useful in order to avoid the effect of other organic compounds released from cement by the action of the superplasticizer. For BET specific surface area measurements it is important to avoid pre-drying at over 60 °C, as otherwise ettringite can decompose and strongly increase the surface area. In order to evaluate pore solution chemistry correctly the aqueous phase must be extracted without dilution. In addition, the fluidity performance of many cements in superplasticized concretes can be changed simply by passage through a storage silo, for reasons which are not yet understood.

Contents

1. Introduction

The understanding of interactions between cement and superplasticizers (SP) has been a big concern in the field of cement and concrete science. There have been numerous studies on this topic [1–5]. However, obviously some studies contain obscure points from the viewpoint of reproducibility and appropriateness of analytical methods. In this review, fundamental interaction mechanisms between cement and SP are summarized and basics of analytical methods relating to them are critically reviewed. Although everyone may know the importance of these analytical methods, the number of researchers who know the detailed conditions or requirements for such measurements may be limited.

2. A summary of basic analytical methods and the fundamental working mechanisms of SP

2.1. Amount adsorbed

In general everyone will agree with the simple concept that superplasticizers or plasticizers work as a dispersants mainly after

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their adsorption on the surfaces of the solid phases. This is demonstrated by the simple observation that, although poly-ethylene glycols do not have a dispersing effect on their own, they can be made to work as dispersants by giving them the ability to adsorb on cement surfaces through their attachment to carboxylic groups in polycarboxylate-type SP (PC). Similar observations can be made for sulfonate type SP. Therefore many researchers try to evaluate the amount of SP adsorbed on cement solids, but there are often problems with such measurements. In many cases, PC adsorption is evaluated by means of total organic carbon analyses (TOC), but this can be misleading. An example will be discussed below. But first we will deal with the important issue of surface area.

2.2. Specific surface area of solid phase

As long as a PC works as a dispersant after adsorption, it is easy to imagine that the dispersing performance will be to some extent proportional to the amount adsorbed or the adsorbed surface density. If so, the specific surface areas (SSA) of the solid phases present will significantly affect the performance. If the overall SSA is doubled, it seems natural to think that double amount of superplasticizer will be required to keep the same adsorption density and thus to show the same dispersing performance. Therefore, the SSA of the solid phases is another basic factor needed in the analysis of the interaction between cements and SP. This presents another measurement problem: it is important to understand what each method measures, and the effects of sample preparation on the results.

By combining two factors, some researchers, including the author, have been emphasizing the importance of the amount of PC adsorbed per unit surface area of hydrates [5]. In addition to this basic parameter, other factors affecting the performance of SP should be discussed. Surface potential or steric hindrance or depletion effects may be important [6,7]. However, if one does not first pay attention to the amount of SP adsorbed per unit surface area of hydrates, one cannot assess the importance of the other proposed mechanisms. The author does not intend to deny the importance of other factors but just to suggest that they should be discussed separately and with appropriate evidence. Under some conditions they may be important, but under other conditions they can be neglected. In Table 1, some examples of such factors are listed.

2.3. Solution chemistry

Treating the amount of SP adsorbed per unit surface area of hydrates as the principal factor, the next most important factor to be considered is solution chemistry. If the solid phase remains constant, the adsorption behavior of SP can be significantly affected by changes in solution chemistry because the adsorption occurs through the interaction between anionic functional group of SP and positively charged sites on the hydrate surfaces [5]. Therefore, the evaluation of the solution chemistry of cement paste is indispensable, but it also presents another problem. The solution chemistry of fresh cement paste is mainly controlled by the equilibrium solubilities of portlandite and gypsum and the concentration of dissolved alkalis. Of course, the liquid phase is not completely at equilibrium with any given solid phases during the active period when hydration reactions of aluminate and alite are proceeding, even if the rates are relatively moderate. But, assuming basic solubility equilibria of portlandite and gypsum in alkali solutions, it is necessary to pay attention to the sample preparation methods used for solution chemistry measurements, such as extraction from paste or dilution of paste.

Table 1
Examples of fundamental factors that can influence interactions between cement and SP (other than the amount adsorbed and the SSA of the hydrates).

Category	Fundamental factor
Physical factors	Particle size distribution Morphology of particles
Chemical factors	Mineral phase and type(s) of surface(s) Absorption of SP into hydrates (coprecipitation) Charge density given by SP Steric chemical structure of PC, e.g., side chain length or main chain length

2.4. Overlooked characteristics of cement

There are many published studies in which the characterization of cement seems insufficient. In Table 2, known cement factors affecting the performance of SP are listed [5]. In order to ensure the reproducibility of experiments, each characteristic listed should be evaluated in some way, although it is often not easy. Beyond those known factors shown in Table 2, there are also some factors that are not yet fully evaluated. One example will be introduced in the following section.

3. Difficulty in the analysis of amount adsorbed

The main problem is contamination by organic components originally contained in the cement. Although it is often not clearly stated, in many studies the amount of SP adsorbed is estimated by comparing the TOC analysis of the solution phase extracted from a cement paste to that of the initial mix water containing the SP. However, the TOC content of the cement is not always taken into account, and, even when it is, it is usually estimated by simple water addition. However, because an SP is a kind of surfactant, it can release some organic compounds from the cement that are not released by pure water. If the organic carbon in the cement is limited to simple grinding aids such as di-ethylene glycol, poly-naphthalene sulfate type SP is not affected when the adsorption is evaluated by UV adsorption because such simple grinding aids do not have comparable UV absorption. However, in the case of PC, when the SP content in the aqueous phase is usually measured simply by TOC, the problem is more difficult to resolve.

In Fig. 1, the adsorption behavior of a kind of PC is shown. For increase in PC dosage beyond a certain point, the adsorption appears to decrease! One possible explanation is the release of organic carbon from the cement by action of the PC solution. In order to confirm this hypothesis, size exclusion chromatograph (SEC) was used instead of TOC. The results are also shown in Fig. 1. By applying SEC, a reasonable adsorption isotherm can be obtained. Besides, additional useful information can be obtained by SEC: larger molecules tend to be preferentially adsorbed. This result clearly indicates the importance of molecular size in controlling the action of PC.

One problem when using SEC is the durability of the columns. The aqueous phase of cement pastes contains various unknown chemicals, which can result in choking of the SEC columns after a limited number of measurements. Precise measurements require a lot of care.

4. Appropriate sample preparation conditions and measurement methods for SSA

There are various methods that can be used to evaluate the SSA of a solid phase. The most popular method in the cement industry is the Blaine method, which makes use of the air permeation resistance of the compacted powder. This may be appropriate for Portland cements, e.g., in order to correlate with strength development. However, it is completely inappropriate for measuring the SSA of hydrated cement because this method does not correctly analyze fine flocculated particles such as most hydrates. A typical Japanese normal Portland cement (NPC) has a Blaine SSA around 330 m^2/kg and BET SSA of 800–900 m^2/kg. The SSA of the solid phase separated from a fresh cement paste still has a similar Blaine SSA but has a greatly

Table 2
Important cement factors affecting the performance of SP[5)].

Mechanism	Factor	Details
SSA	Amount of C_3A	Alumina content
		MgO content
		Cooling rate
	Reactivity of C_3A	Fineness of cement or content of fine grains
		Degree of pre-hydration or carbonation during transportation or storage
		Type and amount of sulfates
		Alkali content and crystalline form of C_3A
		Type and amount of grinding aids, including water
	Interaction with admixtures	Number of carboxylic groups; other organic acids
	Mixing efficiency	Paste, mortar, or concrete
Solution chemistry	Sulfate ion concentration	Type and amount of alkali sulfate
	Intercalation	Formation of “organo-mineral precipitates”
	Order of SP addition	Delayed addition reduces intercalation
	Syngenite formation	Caused by too much soluble potassium
Rheology at low W/C	Fine grains (around 1 μm)	Volume-filling effect between cement particles
Others	Temperature	Affects hydration rates and chemical equilibria
	Agglomeration and deflocculation	Some particles behave as flocculated agglomerates
		Deflocculation results in the release of trapped water in agglomerates
	Proper evaluation of concrete rheology	Rheology or workability of concrete is determined by the particle size distribution of all constituents, as well as the paste rheology

increased BET SSA. This indicates that the Blaine method is insensitive to the increase in initial hydrates, but BET method is sensitive for them.

The BET method using N_2 adsorption is expected to be better for measuring hydrated samples, but there are still some major questions to be answered:

1. SP is not adsorbed in a similar way to N_2 gas. Their adsorption mechanisms – ionic interactions in water and van der Waals forces in a vacuum, respectively – are very different, and steric hindrance can also affect the adsorption of large SP molecules in water. How does this affect our conclusions regarding the “true surface area for SP adsorption”?
2. The effective SSA of a hydrated cement paste may change significantly when the specimen is dried to prepare it for BET analysis.

This last question is important with respect to the sample preparation methodology used before a BET measurement. In general, samples are dried under vacuum at relatively high temperature. But it is well known that cement hydrates are very sensitive to drying. The morphological changes due to drying were beautifully demonstrated by German researchers using an environmental SEM [8]. However, it is very difficult to evaluate the SSA of wet samples. Therefore, the sample must be dried to some degree, but there should be an optimum condition for sample treatment [9]. Among the major cement hydrates, ettringite is apparently the most easily affected by sample preparation. It is well known that the XRD pattern of ettringite disappears on heating at 100 °C. In Fig. 2, the BET SSA of initial hydrates, i.e., the difference between the BET SSA of the paste and the original cement, and the mass reduction due to pre-heating are shown for different pre-heating temperatures. Mass reduction is proportional to pre-heating temperature but the effect on BET SSA is small, below 60 °C. However, beyond 60 °C, BET SSA increases rapidly. In Fig. 3, a correlation between the measurement results of SSA of fresh NPC paste pre-heated at different temperatures and the peak height of ettringite in XRD pattern before pre-heating are shown. The ages of measurement were just after 5-minute mixing and at 2 hours later. There are linear correlations between ettringite amount and BET SSA at each pre-heating temperature and the ratio of BET SSA at 80 to

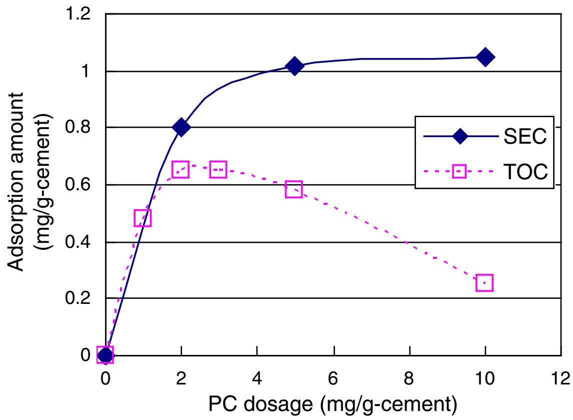

Fig. 1. Comparison of measurement results of PC adsorption in cement paste by using SEC and TOC (W/C = 0.40).

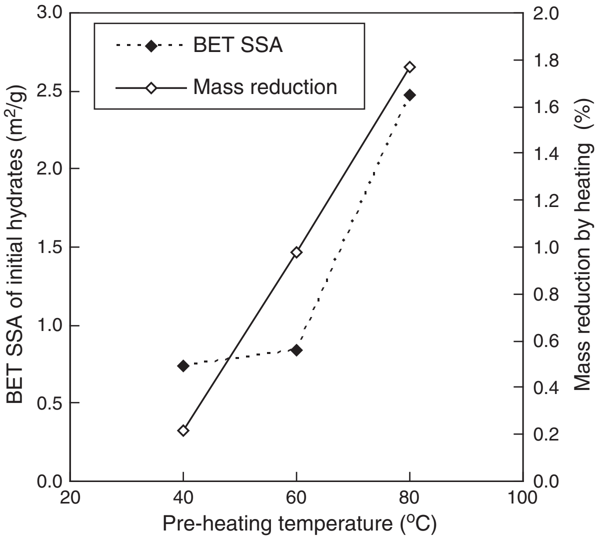

Fig. 2. The effect of pre-heating temperature for BET SSA and mass reduction of initial hydrates formed by mixing with water without SP (paste, W/C = 0.35).

40 °C is around 4. This indicates that pre-heating partially dehydrates or decomposes ettringite and increases its BET SSA by a factor of 4.

Using pure synthetic ettringite, similar increases in BET SSA beyond 60 °C were observed. Portlandite, C–S–H, and gypsum are other major water-bearing phases in fresh cement paste and so their behaviors were also checked. There were no significant effects on BET SSA for any of them in the range of 40–60 °C and only small effects above that temperature, except for gypsum, for which, at 110 °C, the BET SSA increased by a factor of 10, presumably due to dehydration to give β-hemi-hydrate.

Based on the above results, vacuum drying of cement pastes for BET analysis should be done below 60 °C in order to avoid changes in SSA, even though it will take longer.

There are some other interesting observations relative to the SSA measurement of cement. In a cement plant, the same clinker was ground at different temperatures with different amount of water addition. Milling temperature was not controlled (variations were caused by changes in the temperature of the clinker entering the mill). The use of a water spray in the cement milling process is popular because water is thought to work as a grinding aid as well as a coolant. It is important to keep the milling temperature low enough to avoid the formation of too much calcium sulfate hemi-hydrate or reactive anhydrite in order to suppress any false setting tendency. In Fig. 4, the correlation between the milling temperature and the difference between BET SSA measured after pre-drying at 40 and 80 °C is shown. The water addition ratio was controlled at two different values. Regardless of the water addition ratio used, the difference of BET SSA shows a negative correlation with milling temperature. Based on the results reported above for pure phases, it seems that some ettringite must form when the milling temperature is lower. This kind of slight difference of ettringite amount cannot be detected by usual techniques such as XRD.

As is well known, dehydration of gypsum during grinding produces hemi-hydrate. In Fig. 5, the effect of milling temperature on the form of calcium sulfate in NPC is shown. Regardless of the water addition ratio used, with the increase in the milling temperature, the ratio of hemi-hydrate increased and reached 100% at 120 °C. In Fig. 6, the effect of milling temperature on the fluidity of NPC mortar containing a type of PC is shown. With the increase in milling temperature, fluidity increased. Again the effect of water addition seems negligible although the number of data is limited. This may be caused by better suppression of initial C_3A hydration by the presence of more rapidly soluble hemi-hydrate.

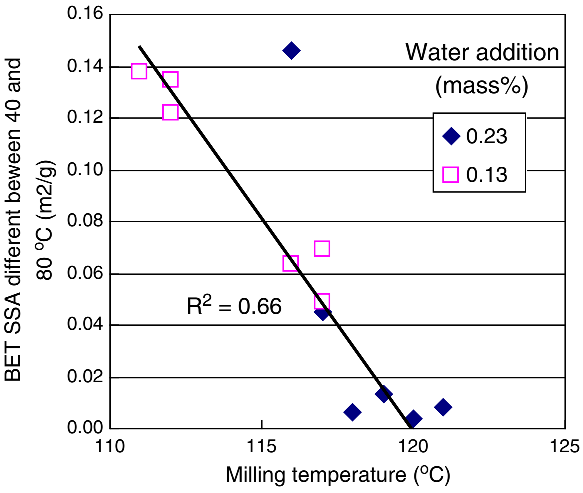

Fig. 4. The effect of milling temperature on the BET SSA difference between 40 and 80 °C of pre-heating temperature during sample preparation (NPC).

5. Solution chemistry change by dilution

It is not easy to get a big-enough amount of sample of the aqueous phase for analysis, especially from cement pastes with low W/C. It may be possible for W/C of 25–30% by using high-speed centrifugal separation. However, for lower W/C or for the case where such specialized separation devices are not available, cement paste is in some cases diluted with water. As explained before, because fresh cement paste is close to equilibrium in the portlandite–gypsum system at a dissolved alkali concentration given by amount of soluble alkalis in the cement plus any alkalis added by the admixtures, any dilution will evidently decrease the alkali concentration, which thus changes the equilibrium of the system. In Fig. 7, the correlation between W/C and ionic concentration of cement paste is shown. Na and K ionic concentrations behaved linearly in log–log plot of W/C and concentration. When W/C increases by a factor of 10, Na and K concentrations decrease by the same factor, due to simple dilution. However, the situation is different for sulfate, hydroxide and Ca ions. For sulfate ions, the decrease in concentration is less than simple dilution because the extra gypsum dissolves. The behavior of hydroxide ion is also non-linearly affected by the dissolution of portlandite. But Ca behaves completely differently and shows a peak

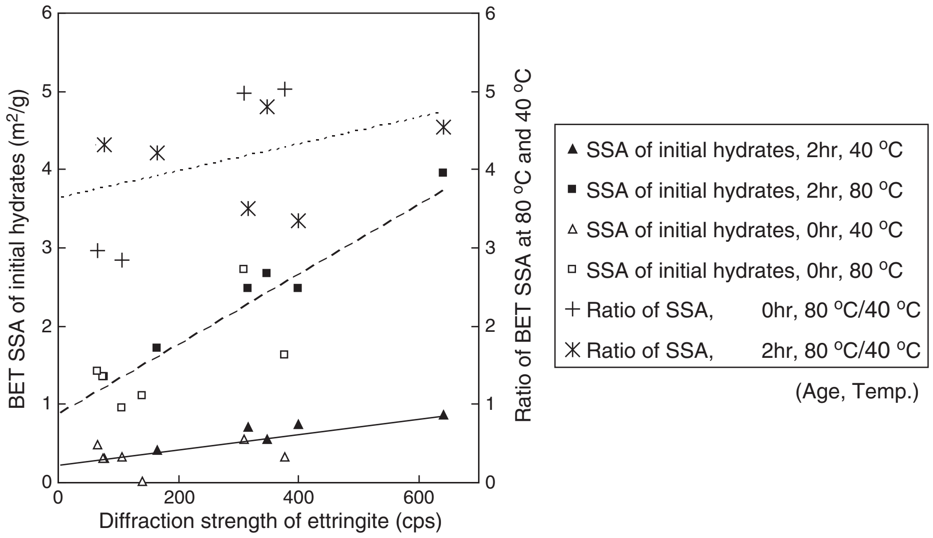

Fig. 3. The correlation between ettringite amount by XRD and BET SSA of initial hydrates (paste, W/C = 0.35).

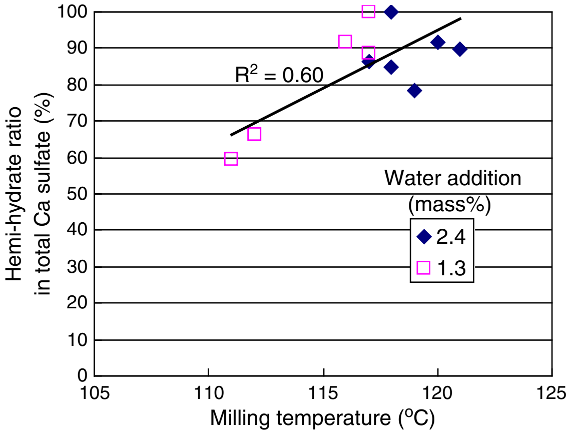

Fig. 5. The effect of milling temperature on the form of Ca sulfate in cement.

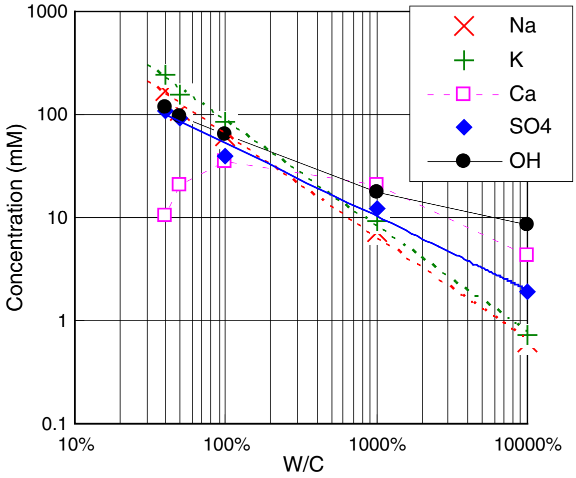

Fig. 7. W/C and ionic concentration of solution phase of cement paste.

concentration around W/C = 100%. Below W/C = 100%, i.e., in the realistic W/C range for actual concretes, Ca concentration decreases with decreasing W/C, which is opposite to the behavior of other ions. One thing required to point out is the effect of formation of syngenite. K concentration in this experiment seems too low to precipitate syngenite. However, once syngenite begins to precipitate, solution chemistry is affected by the solubility equilibrium including syngenite and the behavior of K concentration will be different from the tendency shown in Fig. 7.

Now, it is well established that the adsorption of SP is affected by aqueous ionic concentrations, especially sulfate and calcium. Therefore, judging from the behavior shown in Fig. 7, the aqueous phase should always be extracted from the paste without any dilution. But, of course, it can be diluted after extraction, as is usually required for analysis.

6. An overlooked factor: Changes in concrete fluidity due to cement transportation or storage

Cements can show changes in concrete and mortar fluidity simply after passing through the storage silo in a dispatching center, especially when used with SP. The fluidity change of cement was evaluated in mortar at W/C = 0.35 and including a PC SP. Correlations between the initial flow and the flow at 30 min after mixing are shown in Fig. 8. The chemical compositions of all these lots of NPC are basically the same and would be considered almost exchangeable for average concrete applications without drawing special attention. In the case of N1, the effect of passing through the silo was negligible, but for all the other cements tested the fluidity increased significantly after passing through the cement silo. The major characteristics of each cement were apparently unchanged, but the fluidity performance was different. Clearly, we must have overlooked some important factor. Further study is required to understand the causes of this effect.

7. Conclusions

In order to analyze the interaction mechanisms between cement and superplasticizers, various kinds of basic analytical method are indispensable. In this study, the working mechanisms of polycarboxylate-type superplasticizer were reviewed and detailed requirements for the analytical methods were discussed.

(1) Adsorption: the limitations of using TOC and the advantage of using SEC were explained.
(2) Specific surface area of cement paste: by drying at over 60 °C, ettringite decomposes and the BET SSA increases greatly. It is important to dry samples below 60 °C.
(3) Solution chemistry: by diluting cement paste, the chemical composition of the aqueous phase of cement paste is changed in a non-linear way. In order to correctly evaluate the effect of solution chemistry on the mechanism of superplasticizers, it is

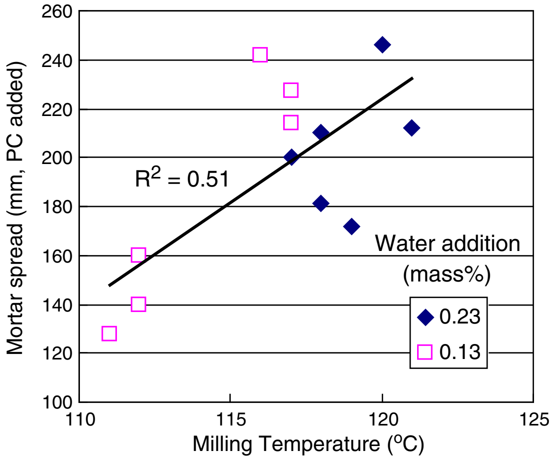

Fig. 6. The effect of milling temperature on mortar fluidity (NPC, W/C = 0.35).

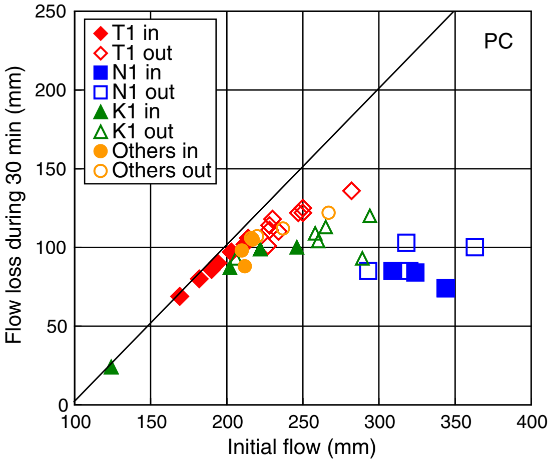

Fig. 8. Comparison of workability of cement before and after passing through silos.

important to extract the aqueous phase from the cement paste without dilution.

(4) The fluidity performance of a cement in superplasticized concretes can be changed significantly simply as a result of passing through a dispatching silo, although no cement compositional changes can be detected by standard analytical methods. Further study is required to understand the cause of this effect.

References

[1] A. Tagnit-Hamou, P.C. Aitcin, Cement and superplasticizer compatibility, World Cement 24 (8) (1993) 38–42.

[2] P.C. Aitcin, C. Jolicoeur, J.G. MacGregor, Superplasticizers: how they work and why they occasionally don't, Concrete International 5 (1994) 45–52.

[3] K. Yamada, S. Hanehara, Working mechanism of polycarboxylate superplasticizer considering the chemical structure and cement characteristics, Proc 11th International Congress on the Chemistry of Cement, 2, 2003, pp. 538–549.

[4] E. Sakai, K. Yamada, A. Ota, Molecular structure and dispersion–adsorption mechanisms of comb-type superplasticizers used in Japan, J. Adv. Concr. Tech. 1 (1) (2003) 16–25.

[5] K. Yamada, A summary of important characteristics of cement and superplasticizers, Prod of Ninth ACI International Conference on Superplasticizers and Other Chemical Admixtures, ACI, SP-262, 2009, pp. 85–96.

[6] K. Yoshioka1, E. Sakai, M. Daimon, A. Kitahara, Steric role of steric hindrance in the performance of superplasticizers for concrete, Journal of the American Ceramic Society 80 (10) (1997) 2667–2671.

[7] S. Chandra, J. Björnström, Influence of cement and superplasticizers type and dosage on the fluidity of cement mortars—part I, Cem. Concr. Res. 32 (10) (2002) 1605–1611.

[8] M. Gretza, J. Plank, An ESEM investigation of latex film formation in cement pore solution Cem. Concr. Res., 41 (2) (2011) 184–190.

[9] K. Yamada, S. Ogawa, S. Suto, M. Yano, S. Hanehara, Measurement condition of BET specific surface area of hydrated cement paste at early ages, Journal of Inorganic Materials, Japan 7 (287) (2000) 268–277, (in Japanese).