

The Effect of Sodium Hexametaphosphate and Trisodium Phosphate on Dispersion of Polycarboxylate Superplasticizer

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ABSTRACT

The high fluidity cement-based material has been widely used in indoor floor, grout, pumping concrete and self-compacting concrete. Efficiently dispersing the cement grains is essential for the practical application of this kind of material. Generally, the retarder can enhance the initial dispersion of PCE system because of the reduced consumption of superplasticizer and free water as well as the delayed formation of the hydration products at the very beginning of hydration. Both sodium hexametaphosphate (SHMP) and trisodium phosphate (TSP) are commonly used retarders. However, SHMP can enhance the initial dispersion of PCE while TSP cannot; this phenomenon cannot be simply explained from the retarding effect. It is proposed in this paper that the different behavior of SHMP and TSP could be related to the water/solid interface performance. The adsorption behavior was analyzed with TOC, ICP and XPS. The adsorption model was then proposed to explain the mechanism. The results show that TSP can reduce the initial dispersing ability of PCE while SHMP can enhance it. Both TSP and SHMP can reduce the adsorption capacity of PCE, but increase the thickness of adsorption layer. This phenomenon indicates that phosphates, which can be quickly precipitated and partly cover the PCE layer, may increase the ineffective adsorption to reduce the initial dispersing ability of the PCE system; on the contrary, for those phosphates, which can be combined with Ca²⁺ and preferentially adsorb onto the surface of cement grains, can avoid the ineffective adsorption to enhance the initial dispersing ability of the PCE system. The results suggest that the dispersing ability of PCE-retarder system is not completely dependent on the total adsorption amount of PCE or the thickness of adsorption layer, but mainly depends on the effective adsorption amount.

1. INTRODUCTION

Currently, cement-based materials with high fluidity have been widely used in indoor floor, grout, pumping concrete and self-compacting concrete, mainly because of its superior workability and highly efficient construction. However, how to disperse the cement particles effectively is essential for the practical application of this kind of material. The comb-type copolymers, known as the polycarboxylate superplasticizer (PCE), are usually employed to achieve the high fluidity of cementitious materials. However, the commercial PCE is a multi-component system rather than a single-component system, which usually consists of PCE and retarder. Although added as a supplementary component, the retarder can significantly enhance the dispersing ability of the superplasticizer. This is mainly attributed to the reduced consumption of both free water and superplasticizer due to the delayed hydration at the very early stage (Li *et al.*, 2012; Lesage *et al.*, 2015).

Poly-phosphate, such as sodium tripolyphosphate and sodium hexametaphosphate (SHMP), has been widely used to enhance the initial dispersing ability of PCE system. However, mono-phosphate, such as trisodium phosphate (TSP) and sodium

hydrogen phosphate, cannot play the same function as the poly-phosphate. The reason that the poly-phosphate can effectively enhance the dispersing ability of PCE system whilst the mono-phosphate cannot is still unclear, and this cannot be simply explained by the retarding effect, because both TSP and SHMP are commonly used as retarders for Portland cement. One possible explanation could be attributed to the difference in the molecular structure of the phosphates, which could result in different performance at the water/solid interface during the very early-stage hydration. As a consequence, different adsorbing behavior of PCE could be expected in the presence of phosphates.

The aim of this paper is, therefore, to study the dispersing mechanism of PCE-phosphate system. Specifically, the fluidity of cement paste was tested in order to evaluate the dispersing ability of PCE-phosphate system. The adsorbing behavior of PCE or phosphate, including the adsorbed amount and the thickness of the adsorption layer, was analyzed in order to assess the performance of the water/solid interface. An adsorption model was then proposed to illustrate the mechanism involved in dispersing PCE in the presence of phosphate. It is anticipated that this study will provide some

guidance on how to choose the right retarder to enhance the dispersing ability of PCE in the future.

2. EXPERIMENTAL

2.1 Materials

Portland cement, 42.5, supplied by Wuhan Yadong Cement Co., Ltd. in China was used in this study. Its chemical composition is shown in Table 1.

Table 1 Chemical composition of the cement

	Loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	CaO	MgO	K ₂ O	Na ₂ O
wt%	3.82	24.08	4.72	2.46	2.31	58.24	1.95	1.02	0.27

A commercially available PCE with solid content of 40 wt% was employed as superplasticizer.

The reagent grade phosphates (made by Sinopharm Chemical Reagent Co., Ltd., China), including TSP (Na₃PO₄·12H₂O, the crystal water was considered in the calculation) and SHMP (Na₆P₆O₁₈), were used as retarders.

2.2 Test Methods

2.2.1 Fluidity of the cement paste

Cement paste was prepared at a water/cement ratio of 0.29 (water: 87 g, cement: 300 g) in accordance with Chinese Standard GB 8077-2008. A flow cone (height 60 mm, top diameter 36 mm and bottom diameter 60 mm) as specified in Chinese standard GB 8077-2000 was used to assess the spread of cement paste. The average of the maximum spreads in two perpendicular directions was reported as the fluidity value.

2.2.2 Adsorption

The solution (20.0 g, PCE or phosphate) and cement (1.0 g) were mixed and stirred for 5 minutes. The suspension was then separated by centrifugation at 3000 r/min for 4 min. Following this, the organic carbon content and the phosphorus content of the upper supernatant were measured with a Total Organic Carbon Analyzer (TOC, Liquid TOC II, made by Elementar, Germany) and an Inductive Coupled Plasma Emission Spectrometer (ICP, Optima 4300 DV, made by Perkin Elmer Ltd., USA), respectively. The solid was then dried in a vacuum drier at 25 °C which was then used for XPS measurement. The amount of adsorbed PCE or phosphate (mg/g-cement) was calculated as follows:

$$\text{Adsorption amount} = V (C_0 - C) / m$$

Where, C₀ is the initial concentration (g/L) of PCE or phosphates before adsorption, and C is the residual concentration (g/L) after adsorption. V is the volume of the solution (mL); m is the mass of the cement (g).

2.2.3 XPS (X-ray Photoelectron Spectroscopy)

The silicon, oxygen, phosphorus and calcium were characterized with an X-ray photoelectron spectrometer (XSAM 800, made by KRATOS, England). Aluminum with an energy resolution of 0.100 eV was used as an anode target ($h\nu=1486.6$ eV) and the XPSPEAK 4.1 was used to process the data.

3. RESULTS AND DISCUSSION

3.1 Fluidity of cement paste

As shown in Fig.1, the fluidity of cement paste with PCE was increased with the increasing dosage of SHMP, but reduced with the increasing dosage of TSP. This result implies that while the SHMP can enhance the dispersing ability of PCE, the opposite is true for TSP.

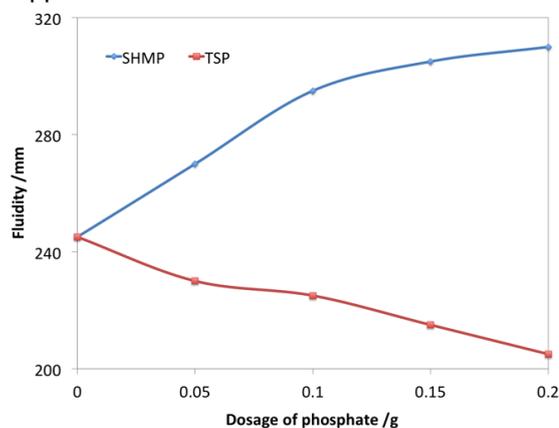


Fig.1 Effect of phosphate on the fluidity of the cement paste with PCE (0.3 wt% of cement)

It is generally believed that the delayed formation of hydration products is the main reason causing the enhanced fluidity of cement paste when both superplasticizer and retarder are present (Ltifi *et al.*, 2011; Lim *et al.*, 2005). Both TSP and SHMP are commonly used as retarders and are, thus, supposed to be able to enhance the fluidity of cement paste. To explain the conflicting results observed in Fig.1, the adsorption behavior was studied and reported in the section below.

3.2 Adsorption behavior

In a single system (i.e. a mixture of cement and only one of the chemicals as mentioned above), as shown in Table 2, the amount of TSP, SHMP and PCE adsorbed by cement was 7.94 mg/g, 7.96 mg/g and 1.05 mg/g, respectively, representing an adsorption ratio of 99.25%, 99.50% and 11.63% accordingly. Both the TSP and the SHMP showed much higher adsorption than that of the PCE. The fact that the vast majority of the phosphates can be adsorbed onto the surface of cement grains indicates that phosphate has a much stronger adsorption capacity than that of PCE.

Table 2 Amount of PCE and phosphates adsorbed by cement

	Single system (0.4g/L)			PCE (0.4g/L) and TSP (0.4g/L)	PCE (0.4g/L) and SHMP (0.4g/L)
	TSP	SHMP	PCE	PCE	PCE
Adsorption amount (mg/g)	7.94	7.96	1.05	0.83	0.41
Adsorption ratio (%)	99.25	99.50	11.63	10.39	5.12

In a binary system (i.e. a mixture of cement with PCE and one of the phosphates), the amount of the adsorbed PCE was reduced in the presence

of phosphate (as shown in Table 2), which indicates that the phosphates can impede the adsorbing process of PCE. The possible reason could be due to the competitive adsorption between phosphate and PCE, because it has been reported that the adsorbed retarders can preferentially occupy the adsorption sites on the surface of cement grain, making them unavailable for PCE (Bey *et al.*, 2014). As a result, the presence of phosphate would obviously hinder the adsorption process of PCE.

It is generally believed that with the same type of PCE, the less the amount of the PCE being adsorbed, the weaker the dispersing ability would be expected. Based on this theory, one could easily explain why TSP can reduce the dispersing ability of PCE-TSP system. However, using the same theory, the enhanced (instead of reduced) dispersing ability of the PCE in the presence of SHMP cannot be explained. Obviously, different PCE dispersing mechanism might have taken place in the presence of different retarders, which could most likely be related to the adsorption layer as discussed below.

3.3 Adsorption layer

The adsorbed PCE or phosphate, which exists on the surface of cement particle as an adsorption layer, can cover the silicon layer of the surface of the cement grains. This can, subsequently, reduce the intensity of photoelectron of silicon (Rudraker *et al.*, 2009). Therefore, the thickness of the adsorption layer can be inferred from the results of XPS data of silicon as follows (Peng *et al.*, 2005; Zheng *et al.*, 2008):

$$I(b) = I_0 \exp[-b/\lambda(E_k)] \quad (1)$$

$$\lambda(E_k) = 49E_k^2 + 0.11(E_k)^{1/2} \quad (2)$$

$$E_k = h\nu - E_b \quad (3)$$

Where, I_0 : Initial photoelectron intensity; $I(b)$: photoelectron intensity after the photoelectron goes through the adsorption layer; b : thickness of adsorption layer, nm; E_k : photoelectron kinetic energy after the photoelectron goes through the adsorption layer, eV; E_b : electron binding energy, eV.

Table 3 XPS data of silicon

	Blank	TSP+PCE	SHMP+PCE	PCE
$h\nu$ (eV)	1486.6	1486.60	1486.60	1486.60
E_b (eV)	101.98	101.97	101.54	101.39
Height Counts	1470.7	749.95	774.44	1013.12
FWHM (eV)	2.72	2.03	2.00	2.62
I_0	4000.4			
$I(m)$		1522.40	1548.88	2654.37
I/I_0		0.38	0.39	0.66
E_k		1384.63	1385.06	1385.21
$\lambda(E_k)$		4.09	4.09	4.09
adsorption layer (nm)		3.95	3.88	1.68

XPS data of Si2p is presented in Table 3. The strongest intensity of photoelectron can be observed in the blank sample (i.e. in the absence of any chemical admixture), and the decreased intensity of photoelectron in the presence of PCE or PCE-phosphate system indicates the existence of adsorption layer on the surface of cement

grains. It is easy to find that the presence of phosphate, both TSP and SHMP, can increase the thickness of adsorption layer, which illustrates that the phosphate in PCE system can establish a thicker adsorption layer than that of the single PCE system. This result indicates that a thicker adsorption layer can be formed with the less adsorption amount of PCE which was proved in previous discussion. It was reported that a thicker adsorption layer could result in a stronger dispersing ability of PCE (Zhang *et al.*, 2007; Lv *et al.*, 2012). In that case, the increased adsorption layer can be used to explain the enhanced dispersing ability of PCE-SHMP system. However, the opposite dispersing results cannot be explained by the same theory. It is inferred that the reason is most likely related to the composition and structure of the adsorption layer which is illustrated by a dispersing model below.

3.4 Dispersing model

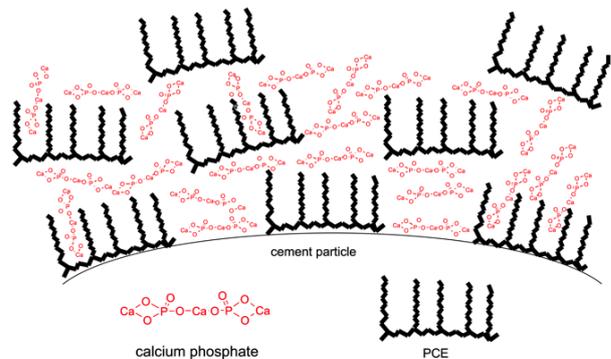


Fig.2 Schematic diagram of dispersing model of PCE system with TSP

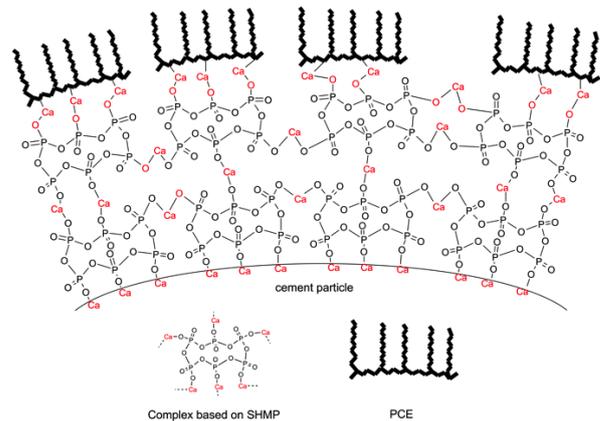


Fig.3 Schematic diagram of dispersing model of PCE system with SHMP

In the PCE-TSP system, the precipitation of calcium phosphate can be formed immediately. This is because TSP can be precipitated with Ca^{2+} in solution at a very low concentration due to the low solubility product constant (K_{sp}) of the calcium phosphate (which is 2.07×10^{-29} at the room temperature) (Dean, 1999). It is well known that the pH value of the cement paste can exceed 12 at the very beginning, which results in about 0.001-0.005

mol/L of Ca^{2+} in solution. Thus, the precipitate can be formed almost at the same time as the release of Ca^{2+} from the surface of cement grains (Lupu *et al.*, 2005), which explains why the adsorption ratio of TSP is more than 99%. Therefore, it is evident the adsorption layer of the PCE-TSP system should consist of a mixture of calcium phosphate and PCE polymer, as shown in Fig.2.

In the PCE-SHMP system, SHMP can be combined with Ca^{2+} rather than be precipitated with Ca^{2+} . The released hexametaphosphate ions can be combined with the superficial Ca-O to form the complexes to accelerate the adsorbing process (Tan *et al.*, 2015); the combined SHMP also can be combined with Ca^{2+} in solution. The Ca^{2+} can be combined with at least two hexametaphosphate ions; in that case, a net structure can be formed. At the same time, Ca^{2+} also can be combined with carboxyl groups of PCE. Through the combination of Ca^{2+} , SHMP can adsorb onto the SHMP layer, and PCE also can adsorb onto the surface of the SHMP layer. Therefore, it is inferred that the adsorption layer containing a phosphate net structure inside and a PCE layer outside can be formed, as shown in Fig.3.

On the other hand, it has been agreed that steric hindrance, offered by the long side chain of PCE, provides the main function to disperse the cement grains. In fact, the dispersion mainly depends on the amount of the PCE adsorbed on the most outer surface of the grain (S-PCE). If the long side chain of PCE were wrapped or covered by the hydration products or precipitates, it cannot be stretched into solution to provide the steric hindrance efficiently; the wrapped or covered PCE would be invalid for the dispersion. Generally, the more S-PCE, the stronger dispersing ability could be formed.

In the PCE-TSP system, TSP could be precipitated with Ca^{2+} on the surface of S-PCE, as shown in Fig.2. In that case, the S-PCE would be partly covered by the precipitates. The PCE adsorbed at the inner layers and covered by the precipitates, cannot provide the dispersing ability efficiently, which explains the reduced dispersion of PCE-TSP system. As a consequence, in the case of PCE-SHMP system, SHMP can be preferentially combined with Ca^{2+} in solution and Ca-O structure on the surface of cement grains. The adsorbed PCE, thus, almost exists on the surface of the SHMP layer, as shown in Fig.3. PCE in solution also can continuously adsorb onto the SHMP layer to form a S-PCE layer over time. It is, therefore, concluded that the main reason for the increased dispersing ability of PCE-SHMP system is the formation of the multiple-adsorption layer containing several SHMP layers inside and a PCE layer outside, which increases the dispersion efficiency of the PCE adsorbed on the surface of cement grains. The current study would suggest that the dispersing ability of PCE system is decided by the effective adsorption amount rather than the total adsorption amount of PCE.

4 Conclusion

The presence of trisodium phosphate can reduce the dispersing ability of PCE system, but sodium hexametaphosphate can enhance the dispersing ability. Both TSP and SHMP can impede the adsorbing process of PCE and increase the thickness of adsorption layer. However, TSP covers the adsorbed PCE which reduces the dispersing ability of the PCE system, while SHMP can complex with Ca^{2+} and preferentially adsorb onto the surface of cement particle, which would not hinder the dispersion ability of PCE and can enhance the dispersing ability of the PCE system. The results suggest that the dispersing ability of PCE-retarder system is not completely dependent on the total adsorption amount of PCE or the thickness of adsorption layer, but mainly depends on the effective adsorption amount.

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