Cement and Concrete Research 115 (2019) 43–58

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Comparative study of two PCE superplasticizers with varied charge density in Portland cement and sulfoaluminate cement systems

Hongwei Tian[a,b], Xiangming Kong[a,*], Tong Su[b], Dongmin Wang[b]

[a] Key Laboratory of Civil Engineering Safety and Durability of China Education Ministry, Department of Civil Engineering, Tsinghua University, Beijing 100084, China
[b] Department of Chemical Engineering, China University of Mining & Technology, Beijing 100083, China

ARTICLE INFO

Keywords:
Superplasticizers (D)
Charge density (D)
Fluidity (A)
Hydration (A)
Cement (D)

ABSTRACT

Two PCEs with acid to ether monomer ratio of 4 and 22, marked as PCE4 and PCE22 respectively were prepared via radical polymerization in order to study their impacts on fluidity and early hydration in Portland cement (OPC) and Sulfoaluminate cement (SAC) systems. Dynamic light scattering measurement reveals that hydrodynamic radius of PCE22 is more sensitive to Ca^{2+} from being crosslinked. Fluidity tests show that PCE22 exhibits lower initial fluidizing effect than the lower charged PCE4 in OPC paste because of the inter-polymer crosslinking by Ca^{2+} bridging effect while the opposite comparison is observed in SAC paste due to the lower $[Ca^{2+}]$ in SAC paste than in OPC paste. PCE22 is found to significantly depress the early formation of AFt crystal in SAC paste, indicated by the results of XRD, TGA, BET and calorimetric tests. Thus, PCE22 behaves better in fluidity retention than PCE4 in SAC paste.

1. Introduction

Ordinary Portland cement (OPC) is by far the largest cementitious material used in concrete and mortar. In parallel, specialty cements, such as sulfoaluminate cement (SAC) are attracting increasing attention [1–8], not only due to their superior technical properties such as fast early strength development, lower shrinkage, high frost-resistance and corrosion-resistance [1,2,9,10], but also due to the much lower environmental impacts of the manufacturing process of SAC, including lower energy consumption and lower CO_2 emission etc. [2,11,12].

Superplasticizers, particularly polycarboxylate superplasticizers (PCE) have become one of the indispensable components in the formulations of modern concrete. PCE is a group of *comb*-like polyelectrolyte, usually with poly (acrylic acid-*co*-acrylic ester/ether) as backbone and polyethylene oxide (PEO) as side chains [13]. When PCE is mixed into fresh cement paste (fcp), deprotonation of carboxyl groups in alkaline condition leads the backbone of PCE molecules negatively charged and the PCE molecules are adsorbed onto the surface of various mineral phases in fcp, such as the surface of cement grains, hydration products like AFt etc., mainly due to the electrostatic interaction between the mineral surfaces and PCE molecules [14,15]. The adsorbed PCEs provide electrostatic repulsion and/or steric hindrance between the mineral surfaces. In this way, the cement grains are well dispersed in fcps and the fluidity of fcps is greatly increased by the addition of PCE [16–18].

Substantial progress has been made in the last decades in PCE technology and PCE science [9,16,17,19–22]. However, most of the studies are targeted to OPC systems [16,17,19–21]. With increasing consumption of SAC, tailor-made PCE superplasticizers for SAC system are in urgent need. It is well known that OPC is mainly composed of four major clinker phases and additional sulfate carriers such like gypsum, anhydrate and hemihydrate, while the major composition of SAC is calcium sulfoaluminate, sulfate phases and C_2S etc. [1,2,5,7]. Thus, the charging features of the surfaces of OPC grains and SAC grains must be different and as a result the adsorption behavior of a given PCE accordingly varies in the two cement systems. In addition, the hydration kinetics as well as the hydration products of the two types of cement are entirely different. The setting time of OPC paste is usually several hours while that of SAC is usually from several minutes to several tens of minutes [1,23–28]. The major hydration product of OPC is C-S-H while that of SAC is AFt crystals. It has been recognized that the initially formed AFt crystal phase adsorbed a large amount of PCE molecules due to its highly positive charging feature and huge specific surface area. Thus, the adsorption of PCE in SAC pastes could be much more than that in OPC pastes due to the vast early formation of AFt crystals in SAC pasts. Therefore, the PCE superplasticizers developed for OPC systems usually do not work as well in SAC systems, expressed by the high dosage of PCE, lower initial fluidity of fcps and hard control of

---

[*] Corresponding author.
E-mail address: kxm@mail.tsinghua.edu.cn (X. Kong).

https://doi.org/10.1016/j.cemconres.2018.10.003
Received 25 September 2018; Accepted 10 October 2018

Table 1
Chemical and mineralogical composition of Ordinary Portland cement. (*wt*%).

Chemical composition								Mineralogical composition						
CaO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	Na_2O_{eq}	f-CaO	LOI	C_3S	C_2S	C_3A	$C_2(A,F)_2O_5$	$CaSO_4$	$CaSO_4 \cdot 0.5H_2O$	$CaSO_4 \cdot 2H_2O$
65.1	22.0	3.4	4.5	2.4	0.5	0.9	1.2	63.5	16.9	4.2	10.1	1.0	1.0	2.7

Table 2
Chemical and mineralogical composition of sulfoaluminate cement. (*wt*%).

Chemical composition										Mineralogical composition				
CaO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	MgO	Na_2O_{eq}	TiO_2	K_2O_{eq}	LOI	$C_4A_3\bar{S}$	C_2S	C_3A	$C_{12}A_7$	$CaSO_4$
48.6	19.5	1.0	15.0	9.2	4.5	0.3	0.7	0.4	< 0.01	31.6	38.9	8.9	4.5	8.6

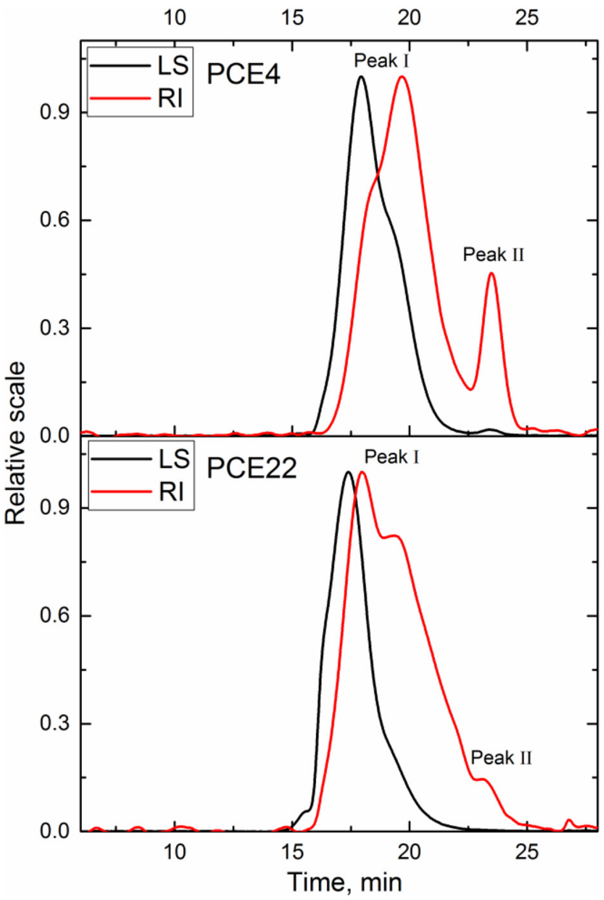

Fig. 1. GPC chromatograms of the two PCEs (LS: light scattering, RI: refractive index).

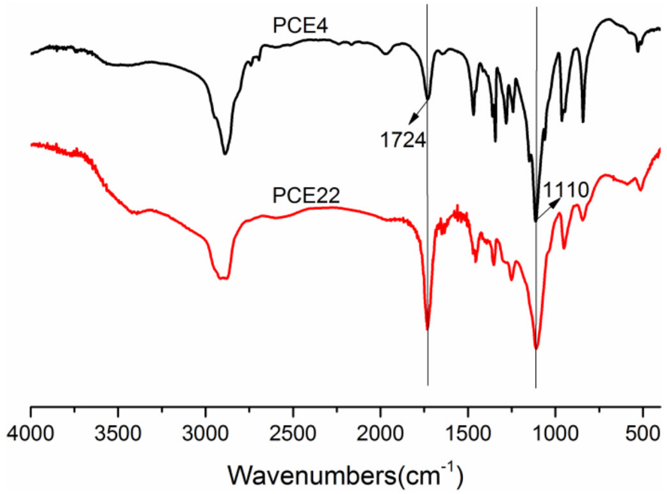

Fig. 2. FTIR spectra of the dialysis purified PCE polymers.

the fluidity loss over time [9,29,30].

Taking all these into consideration, in this paper, we synthesized two typical PCEs with varied charge density and investigated the fluidizing effect of the two PCEs in OPC as well as in SAC systems. The PCEs were prepared by copolymerizing acrylic acid (AA) and α-methallyl-ω-hydroxy poly (ethylene glycol) (HPEG) monomers via radical polymerization. By varying the monomer ratio of AA to HPEG, the charge density of the obtained PCEs could be tuned. The working mechanism of the PCEs were studied by means of adsorption measurement, BET surface area measurement of the particulate matters in hydrating cement pastes, XRD, calorimetry etc. The objective of this paper is to lay down a fundamental principle for designing a PCE superplasticizer for different cement systems.

2. Experimental

2.1. Materials

2.1.1. Cement

Ordinary Portland cement 42.5R compliant with the Chinese standard GB 175–2007 was used. The rapid-hardening sulfoaluminate cement was produced by Polar Bear Building Materials Co., Ltd. Tangshan, China. The chemical and mineralogical compositions of the two cements were listed in the Table 1 and Table 2, determined by XRF and the quantitative XRD Rietveld method. The specific surface areas of

Table 3
The characteristic parameters of the PCE polymers.

Polymer	Molar ratio of monomers AA to HPEG fed during synthesis	Molar ratio of the repeating units AA to HPEG in the synthesized PCEs determined by ^1H NMR	Mass fraction of polymer in the solute part of the synthesized samples (%)	Mw (g/mol)	DPI (Mw/Mn)	Charge density (μeq/g, pH = 12)
PCE4	4	4.14	86.1	58,500	1.870	− 1032
PCE22	22	21.27	95.8	94,500	1.422	− 4052