

Early calcium monocarboaluminate hydrate formation in cement paste: effect of polycarboxylate type admixture

Jiang Yaqing¹ Zhang Sijia^{1,2} Liu Xiaoyan¹ D. Damidot²

(¹School of Mechanics and Materials Science, Hohai University, Nanjing 210098, China)

(²Civil and Environmental Engineering Department, École des Mines de Douai, Douai 59500, France)

Abstract: Effects of polycarboxylate type admixture (PCA) on calcium monocarboaluminate hydrate (AFmc) formation in hydrated cement paste containing limestone filler (LF) are investigated by the Fourier transform infrared spectroscopy (FTIR), the scanning electron microscopy (SEM), the derivative thermogravimetric (DTG) analysis and the adsorption amount measurement. Experimental results indicate that AFmc forms during the initial hydration period of cement as early as 15 min. It is found that PCA accelerates the early age AFmc formation and enhances cement hydration by promoting C₄AF hydration at the early age, and, as a consequence, the iron associated AFmc phase forms more readily. The phenomenon is not observed when PCA is replaced by a naphthalene formaldehyde sulphonate condensate water reducer. Compatibility between PCA and cement is modified due to the presence of AFmc along with ettringite (AFt), which results in a less adsorption amount of PCA on the surface of cement minerals. As a kind of high-range water reducer, PCA may be the preferred choice for concrete containing LF.

Key words: cement; high-range water reducer; limestone; ettringite; calcium monocarboaluminate hydrate

Polycarboxylate type admixtures (PCA) and limestone filler/addition are two beneficial constituents in modern concrete^[1–3]. Investigations on the effects of PCA or LF on hydration of cement and properties of fresh and hardened concrete has been reported^[4–5]. Zingg et al.^[6] studied the interaction between PCA and cement containing different C₃A amounts and found that in terms of optimization of the molecular architecture, good workability of concrete can be achieved by the addition of highly charged PCA with long side chains. Also, PCA can accelerate the formation of early ettringite (AFt) and calcium monosulfoaluminate hydrate (AFm)^[7].

Thus PCA is more compatible with cement than naphthalene formaldehyde condensate type water reducer because of a less positive zeta potential and a less adsorption amount of AFm than C₃A^[8]. Both Portland-limestone cements and cements blended with up to 5% ground limestone are the most widely used cements in Europe and other countries^[4]. As it is known, the limestone filler seems to favor crystallization

of calcium monocarboaluminate hydrate (AFmc) rather than AFm^[4–6]. Little literature involved in PCA-AFmc interaction is available. So it is of significant importance to explore early AFmc formation in hydrated cement paste containing LF and PCA for better control of PCA-cement compatibility and early age performance of concrete.

1 Experimental Program

1.1 Materials

Cement: A kind of Portland cement equivalent to Chinese P. I 52. 5.

Limestone filler: A commercially available pure material with a particle size finer than 30 μm.

Chemical admixtures: Self-made polycarboxylate type admixture and a kind of commercial naphthalene formaldehyde sulphonate condensate water reducer.

Water: Deionized water.

1.2 Methods

Specimens fabrication: The specimens of cement pastes with a water-cement ratio of 0.3 and a PCA dosage of 0.2% of cement, and those of blank cement paste with the same water-cement ratio are mixed in a laboratory maintained at 20 °C and 90% RH. 1 g of each paste is taken at 15, 30, 60 min, respectively, and then mixed with 40 mL ethanol. Solids and liquids are separated using a hydro-extractor. Remaining pastes are crushed into small pieces (typically 4 to 5 mm in size) after 24 h and 3 d, and then they are removed and stored in ethanol, to replace the water remaining in the specimens. Subsequently, they are dried at 60 °C in an oven.

Scanning electron microscopy: Specimens are dried again in a vacuum drier and surfaces are sprayed with gold before testing.

Thermal analyses: TGA and DTG analyses are performed on the samples hydrated for 15 min and 3 d (heating rate of 10 °C/min, up to 900 °C). The amounts of AFt and calcium carbonate are calculated from TG curves as follows:

$$W_{AFt} = W_{LAFt} \frac{M_{AFt}}{nM_H} \quad (1)$$

$$W_{CaCO_3} = W_{LCaCO_3} \frac{M_{CaCO_3}}{M_{CO_2}} \quad (2)$$

where W_{LAFt} and W_{LCaCO_3} are weight losses occurring during AFt dehydration and CaCO₃ decomposition, respectively. M_{AFt} , M_H , M_{CaCO_3} and M_{CO_2} are the molecular masses of ettringite, water, calcium carbonate and carbon dioxide, respectively. The amount of monocarboaluminate is indirectly

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calculated via the calcite consumed.

Fourier transform infrared spectroscopy: The KBr pellet methodology is used to prepare the solid samples, which are covered at frequencies from 4 000 to 400 cm^{-1} .

Adsorption amount measurement: The amount of PCA adsorbed on cement is measured with an ultraviolet and visible spectrophotometer (UV-2450, Shimadzu Corporation). The wavelength of 240 nm is selected for quantitative analysis. PCA solutions with various concentrations and 0.5 g of cement are mixed by a magnetic stirrer for 10 min. The water to cement ratio is 4 000%. Solutions are separated using a hydro-extractor. The concentration of PCA remaining in the solution is measured and the amount of PCA adsorbed is calculated. The adsorption isotherms are drawn with the value of adsorption and the equilibrium concentration.

2 Results and Discussion

2.1 FTIR spectra of hydrated cement

Experimental results of FTIR spectra are shown in Fig. 1.

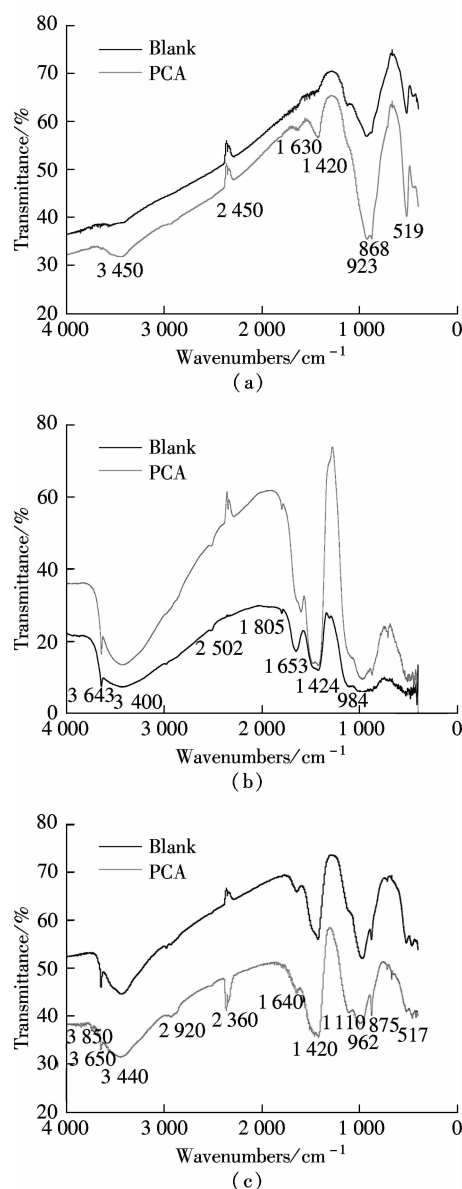


Fig. 1 FTIR spectra of cement pastes. (a) Hydrated for 15 min; (b) Hydrated for 1 d; (c) Hydrated for 3 d

Weak frequencies, peaked at 3 650 cm^{-1} and 3 640 cm^{-1} which are ascribed to OH^- associated $\text{Ca}(\text{OH})_2$, are detected in both pastes with and without PCA when the hydration lasts for 15 min. The bands are sharper for pastes hydrated for 1 d and 3 d than those hydrated for 15 min. A peak frequency exists due to the vibration of $\nu_3\text{-SO}_4^{2-}$ between 1 100 cm^{-1} and 1 200 cm^{-1} , which supports the evidence for the presence of AFt. The center of an AFt associated peak shifts from 1 100 to 1 200 cm^{-1} with cement hydration prolongation, which means that AFt gradually forms as gypsum is consumed. Frequencies at 1 600 to 1 650 cm^{-1} are ascribed to $\nu_2\text{-H}_2\text{O}$ in gypsum. None of this typical band is presented in blank cement paste hydrated for 15 min. Whereas a band at 1 630 cm^{-1} indicates that PCA accelerates AFt formation even at the initial hydration period of the cement. As is known, the quantity of AFt is almost constant after 24 h of hydration. So it can be seen from Fig. 1(c) that gypsum associated frequencies become flatter for specimens of 3 d hydration, which shows that no free gypsum exists in the hydration system. The strong IR frequencies at 1 420 and 1 424 cm^{-1} are typical bands of $\nu_3\text{-CO}_3^{2-}$. Sharp bands at 875 and 868 cm^{-1} are ascribed to $\nu_2\text{-CO}_3^{2-}$. Obviously, limestone addition changes the early hydrates assemblage of Portland cement by the formation of AFmc.

The FTIR spectra of hydrated cement clearly show that PCA boosts the dissolution-precipitation process of C_3A by the formation of more AFt and AFmc.

2.2 Microstructure of cement hydrated for 1 d

The SEM pictures of cement pastes hydrated for 1 d are shown in Fig. 2. Aluminates in cement containing limestone addition tend to react with both gypsum and calcite simultaneously at an early age of hydration. It is proved by the evidence of AFt and AFmc observed in the blank paste hydrated for 1 d. The microstructure of blank paste and the EDS spectrum of AFmc also support the hypothesis (see Fig. 2(a)). But PCA changes the morphology and hydrates assemblage to some extent. Iron is detected in cement pastes when it is dispersed by PCA (see Figs. 2(b) and (c)). Fewer crystals of ettringite can be seen in hardened cement incorporating PCA whether limestone addition is used or not. In other words, PCA can accelerate monosulfoaluminate formation at an early time^[7], and can promote C_4AF hydration, as shown in Fig. 2(c). But, coexisting with LF, PCA does not promote the conversion of AFt to monosulfoaluminate anymore (see Fig. 2(b)). In contrast, naphthalene formaldehyde sulfonate condensate seems to promote AFt formation only. The presence of unhydrated calcite in the naphthalene formaldehyde sulfonate dispersion system (see Fig. 2(d)) supports this argument.

2.3 Quantification of AFt and AFmc phases

A typical DTG curve of Portland cement blended with limestone filler hydrated for 15 min is shown in Fig. 3. The results of DTA are comparable to the results of FTIR. Characteristic peaks of AFt and AFmc are remarkable even if hydration time is as short as 15 min.

The thresholds of AFt and calcite consumed are obtained by Proteus Analysis software. Quantities of AFt and calcite

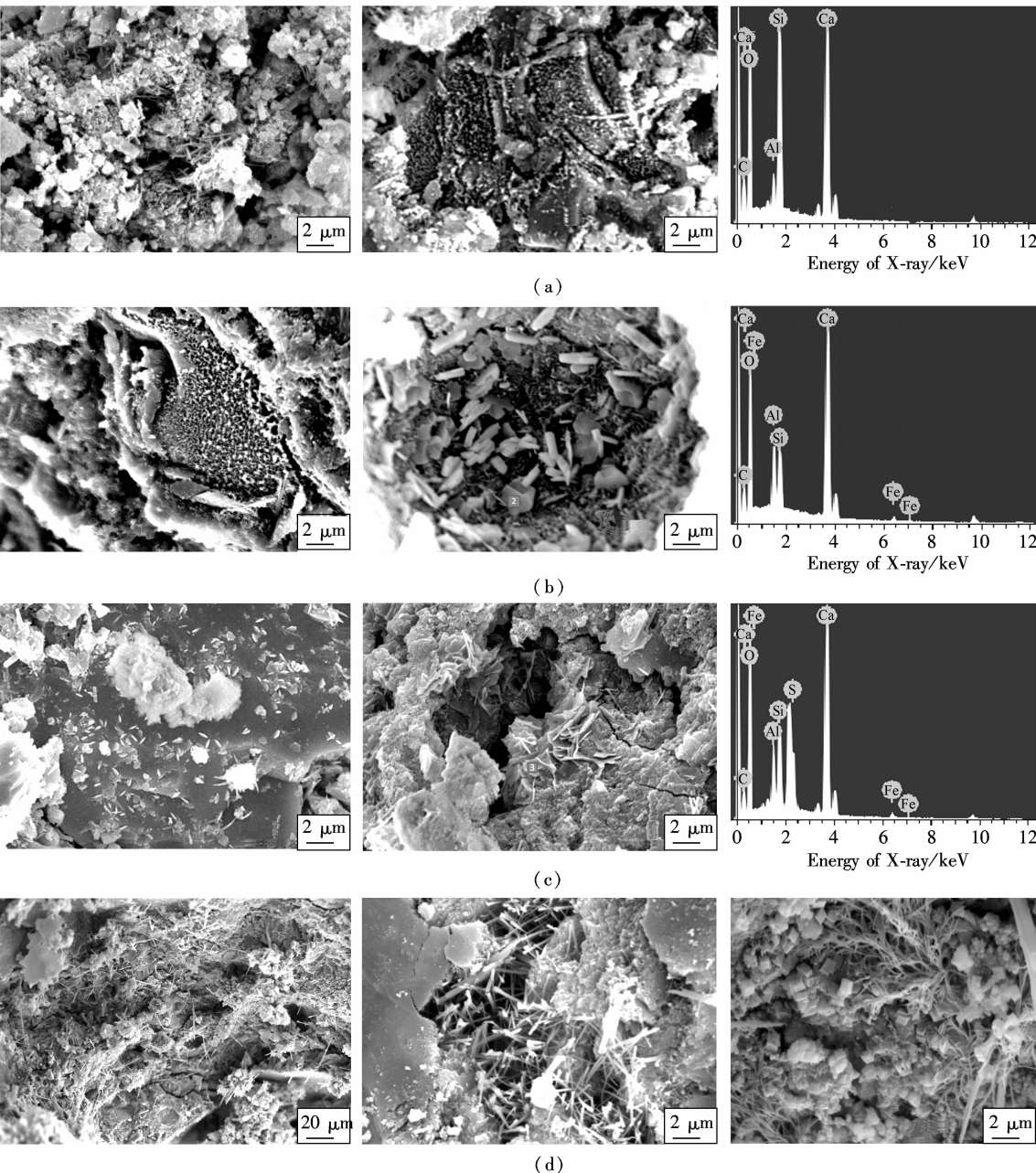


Fig. 2 Microstructure of cement pastes hydrated for 1 d. (a) Blank cement paste with 5% LF; (b) Cement paste with PCA and 5% LF; (c) Cement paste with PCA; (d) Cement paste with naphthalene formaldehyde condensate water reducer and 5% LF

tially hydrated and fresh cement pastes with and without PCA are almost the same. But AFmc in PCA dispersed paste is 28.7%, 43.2%, 33.3% and 37.8% higher than that in blank paste hydrated for 15 min, 30 min, 60 min and 3 d, respectively. PCA can enhance the reaction ability of limestone to C3A.

Tab.1 Calculated amounts of AFt, AFmc and consumed calcite

					%
Paste	Age	W_{AFt}	W_{AFmc}	$W_{calcite\ consumed}$	
Blank	15 min	1.42	2.30	0.40	
	30 min	1.52	2.57	0.45	
	60 min	1.60	3.09	0.54	
	3 d	10.16	8.88	1.56	
PCA	15 min	1.51	2.96	0.52	
	30 min	1.63	3.68	0.65	
	60 min	1.71	4.12	0.73	
	3 d	10.22	12.24	2.15	

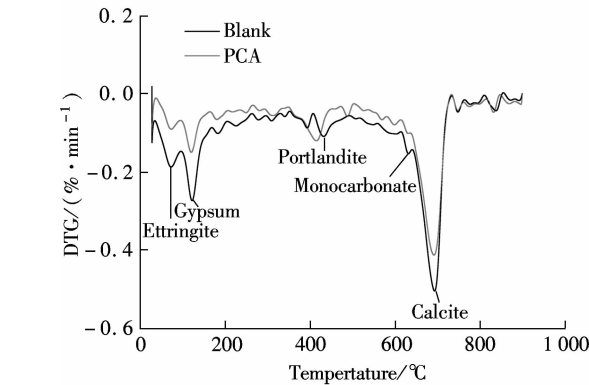


Fig. 3 DTG data of cement pastes with LF hydrated for 15 min calculated according to Eqs. (1) and (2), and quantity of AFmc calculated indirectly are shown in Tab. 1. AFt in ini-

2.4 Adsorption isotherm

The adsorption isotherms of PCA on cement grains with and without LF are shown in Fig. 4. The maximum amounts of adsorbed PCA are obtained by plotting data according to the Langmuir equation, which are 104.2 mg/g (with LF) and 189.4 mg/g (without LF), respectively. It is AFmc that reduces the PCA consumption so that the dispersion effectiveness of PCA is modified. Generally, the surface defects of C_3A whose zeta potential is positive are more than those of silicate minerals; thus the former adsorbs more anionic superplasticizers than the latter. C_3A has the strongest adsorption capacity among all the minerals. As a kind of micro-aggregate, fine calcium carbonate accelerates the hydration reaction of cement at a very early age. C_3A reacts with gypsum to form AFt and the gypsum is depleted in advance. As AFm forms, CO_3^{2-} reacts with AFm to form relatively stable AFmc, or, as SO_4^{2-} is depleted, calcium carbonate reacts with C_3A directly to form AFmc. Therefore, the incorporation of calcium carbonate in cement accelerates the reaction rate of C_3A and the formation of AFmc whose Zeta potential is significantly lower than C_3A , so that the dispersion effectiveness of PCA is enhanced.

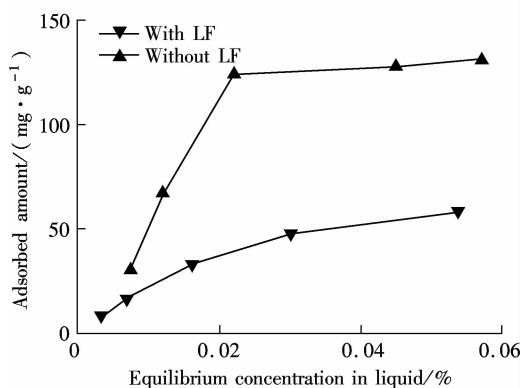


Fig. 4 Adsorption isotherms of PCA

3 Conclusion

The investigation of the promotion behavior of a maleic acid type polycarboxylate superplasticizer used in the present study shows that the early dissolution-precipitation process involving C_3A , C_4AF and calcium sulfate is accelerated by PCA. Consequently, more AFmc exists in a Portland cement hydration system containing limestone filler blend and maleic acid type PCA.

AFmc adsorbs less PCA than C_3A does, and more initial and early AFmc formation is beneficial for modifying the workability and early age performance of cementitious materials.

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聚羧酸减水剂对水泥浆体早期单碳铝酸钙形成的影响

蒋亚清¹ 张思佳^{1,2} 刘小艳¹ D. Damidot²

(¹ 河海大学力学与材料学院, 南京 210098)

(² Civil and Environmental Engineering Department, École des Mines de Douai, Douai 59500, France)

摘要: 利用傅里叶红外光谱 (FTIR)、扫描电子显微镜 (SEM)、热重分析 (DTG) 和等温吸附, 研究了含石灰石填料 (LF) 水泥在掺用聚羧酸减水剂 (PCA) 时, 硬化浆体中单碳型水化碳铝酸钙 (AFmc) 的形成规律. 研究发现, 水泥在水化 15 min 的初始期就形成了 AFmc, PCA 通过促进早期 C_4AF 水化使含铁的 AFmc 更易形成. 以萘磺酸盐缩合物减水剂取代 PCA 时, 未观察到相同现象. 由于浆体中 AFmc 和钙矾石 (AFt) 的共存, 减少了水泥矿物对 PCA 的吸附量, 从而改善了 PCA 与水泥的适应性. 因此, 当混凝土中掺用 LF 时, PCA 应作为首选的高效减水剂.

关键词: 水泥; 高效减水剂; 石灰石; 钙矾石; 单碳型水化碳铝酸钙

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