EFFECT OF EARLY STRENGTH AGENT ON CEMENT SLURRY CONTAINING RETARDER

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Abstract

Retarders have an important regulation effect on the hydration speed and setting time of cement. However, retarders are not conducive to the early strength development of concrete, so use early strength agents to improve their early performance. In this paper, the effects of different amounts of triethanolamine (TEA) and citric acid (CA) on the hydration dynamics and mechanical properties of silicate cement were investigated. The results showed that, as the CA content increases, the setting time of the cement slurry can be effectively prolonged. And the right amount of TEA can not only make the cement reach the early strength, but also increase the compressive strength in the later stage, and control the setting time of the cement paste. TEA shortens the induction period of CA-incorporated cement and increases the heat release rate during cement hydration induction period.

Keywords: Retarders, early strength agents, retarder, hydration dynamics, mechanical properties

1. INTRODUCTION

The different performance of concrete was required due to the special environment and construction conditions, the regulation of the hydration speed and setting time of cement is one of the research focuses in the field. Typically cement setting is controlled by using retarders or accelerators. Triethanolamine (TEA) and Citric acid (CA) are often used as admixtures to regulate the hydration process of cement. Although the combination of the two can lead to increased flexibility in construction methods, there are rarely used in combination.

Ramachandran and Lowery [1] investigated the effect of citric acid, and citrate on Portland cement hydration process respectively, the results showed by heat evolution rates that the hydration of Portland cement is retarded. Other investigations found that the zeta potential of cement decreases with increasing amounts of citric acid added, which can be attributed to the adsorption of citrate ions onto the positively charged surfaces of the Portland cement grains[2]. Researchers also studies have been performed to examine the effects of TEA on hydration of cement. TEA acts as a set accelerator at low dosages and evidently enhances the early strength of cementitious materials [3], while in the case of the dosages of TEA higher than 0.1%, the opposite effects of set-retardation and the strength-loss at both early and late stages have been reported [4]. Previous research indicates that: strong accelerating effect on initial setting time caused by relatively high dosages of TEA ascribed to ettringite formation during accelerated tricalcium aluminate (C_3A, $3CaO{\cdot}Al_2O_3$) hydration but retard that of C_3S[5].

The purpose of this work is to investigate the compensation function of different TEA dosage for the excessive retarding caused by CA. The effects of different amounts of TEA (0.06%, 0.12%, 0.18%, 0.3%, 0.5%) and CA (0.2%) on the hydration dynamics and mechanical properties of silicate cement were investigated.

2. EXPERIMENTS

2.1 Materials

The cement used for this experiment was PII 52.5 ordinary Portland cement conforming to the Chinese Standard GB 175-2007，and the composition of Portland cement are shown in Table 1. Citric acid （CA）and triethanolamine（TEA）are provided by Sinopharm Chemical Reagent Co., Ltd. Other parameters such as setting time and compressive strength are shown in table 1.

Table 1: the composition of cement

Type	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	loss
P·II52.5	64.95	18.31	4.21	2.95	4.22	0.64	0.788	3.21

Table 2:Physical properties of Portland cement

Type	density (g/cm^3)	Specific surface area (m^2/kg)	initial /min	final /min	Flexural strength /MPa		Compressive strength /MPa	
					3d	28d	3d	28d
P·II52.5	3.12	372	180	260	5.10	8.15	30.75	54.04

2.2 Mix proportions and methods

In order to investigate the composite effect of TEA and CA on the hydration of the Portland cement, all cement pastes investigated in this study were prepared at a w/c mass of 0.35, the characteristics of several mixes are shown in table 2.

Table 2: Mixes investigated

Mixes designation	% Citric acid	%Triethanolamine
C02T006	0.2	0.06
C02T012	0.2	0.12
C02T018	0.2	0.18

C02T03	0.2	0.3
C02T05	0.2	0.5

2.3 Characterization

Heat evolution over7days was measured in an isothermal calorimeter (TAM AIR Thermometric) for 5g paste samples. And the constant temperature is 20 °C. A 3 g sample is accurately weighed, placed in an ampoule bottle, and then sealed the ampoule bottle and placed into a calorimeter test 7days.

X-ray diffraction (XRD) was used to analyze the hydration products of cement pastes. XRD patterns were recorded at a scanning rate of 2°/min from 2θ=5° to 2θ=80° with Cu Kα radiation (λ=1.5418 Å) on a D max/RB diffractometer.

The setting time was determine according to GB/T1346-2011 “Test methods for Water Requirement of Normal Consistency, accurate to the minute.

Compressive strengths of the cement cement mortar with difference dosage admixture was measured according to the unconfined compression machine. Each compressive strength value represents the average of the results from 6 specimens tested.

3 RESULTS AND DISCUSSION

3.3 Setting time

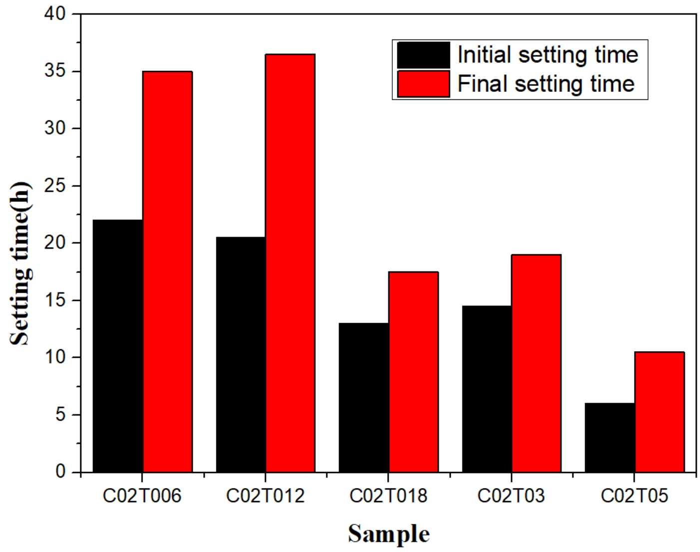


Figure 1: Influence of TEA on the setting time of cement paste containing CA

Fig.1 shows the effects of TEA on the setting time of cement paste containing CA. As can be seen from the figure, CA has obvious delay effect on cement paste, with the increase of TEA, we found the difference trend for the effect of dosage on initial setting time from previous studies[6,7]. When the dosage of TEA is greater than 0.18%, the accelerating effect on setting time are strongly observed. The presence of TEA significantly offset the retarding effect of citric acid. Meanwhile, the setting time is lightly prolong when the TEA dosage reaches 0.3%, However, when the TEA dosage added to 0.5%,the setting time is strongly accelerated and close to the setting time of the control cement paste.

3.2 Compressive strength

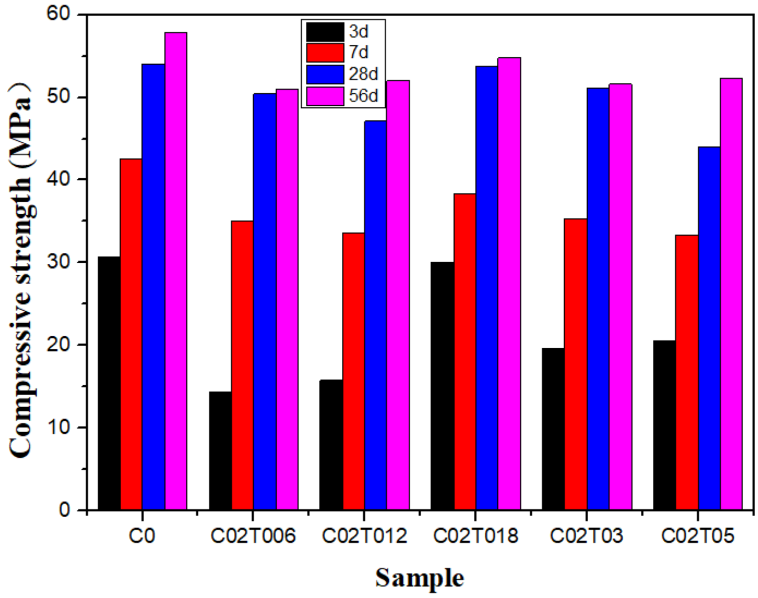
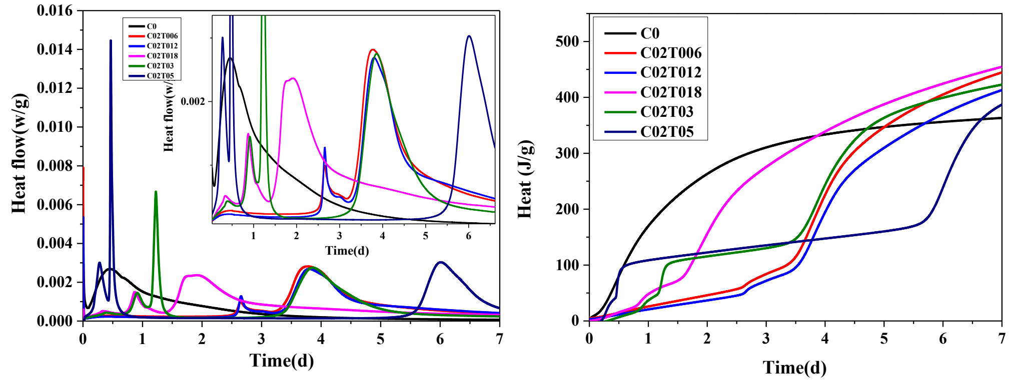


Figure 2: Effect of TEA on compressive strength of cement mortar containing CA

Effect of TEA on compressive strength of cement mortar containing CA is shown in fig.2, CA significantly decreased compressive strength of cement mortar in early age. By 3days of hydration, compare with C0 mortar, the compressive strength of C02T006, C02T012 reduced 53.41%, 48.7%, respectively, and the C02T03, C02T05 also decreased 36.18%, 33.3%. However, it is worth noting that the compressive strength of C02T018 is basically the same as control mortar. At 7 days, the same trend was observed for 3days, C02T018 still has the best mechanical properties among all samples, but the strength of other samples increases rapidly with the passage of hydration time. Ultimately, by 28 days of hydration, all the sample had lightly lower compressive strength than C0 mixture. The relationship between TEA and CA phase content development, reaction kinetics, microstructure, and mechanical properties is a subject of future research.

3.3 Hydration kinetics

Figure 3 shows an example of the relevant impact of addition of CA and variable dosages of TEA on hydration of cement. As shown in fig.3, the exothermic peaks of these samples show different trends to Portland cement hydration process due to TEA and CA added. The heat flow cures of cement is divided into multiple stages with TEA and CA added. The presence of CA significantly retarded the main peak of heat release occurred, Göril Möschner[8] suggested that citrate sorbed onto the clinker surface and formed a protective layer around the clinker grains retarding their dissolution.



(a) Heat evolution **(b) Accumulative heat released**

Figure 3: Isothermal conduction calorimetry of CA with different TEA dosages

In specimen C02T006, two exothermic peaks are monitored during the hydration process, compare with control sample, CA has a retarding effect on the hydration of cement. The first peak was delayed about 48hours. However，the shape of the heat flow curves is significantly influenced by the presence of TEA, the first peak, in initial reaction period, is mainly resulted from ion dissolution and reaction between C_3A and calcium sulfate, usually resulting in formation of Aft. Previous research indicates that TEA accelerates C_3A hydration and C_3A–gypsum reaction by promoting formation of aluminate hydrate and Aft; The second peak, at the end of acceleration period, is mainly resulted from hydration of C_3S, forming C-S-H and calcium hydroxide (CH)[9]. As the TEA dosage increases, the heat flow cures of sample of C02T012 is similar to that of the C02T006. That means the relatively low TEA dosage has lightly effect on the hydration process of cement paste containing CA. When TEA dosage is higher than 0.18%, the hydration heat release rate in initial reaction period is promoted. Meanwhile, with the TEA dosage increase, the accelerating effect on hydration of cement paste is significantly. As the hydration time goes on, the hydration process of the slurry enters a dormant period, and the time of the dormant period increases with the increase of TEA content. Previous research indicates that: the TEA dosage effect on the cement hydration, at small dosage it acts as setting accelerator, at higher dosage it acts as setting retarder, at more higher dosage it acts as setting accelerator once again[10]

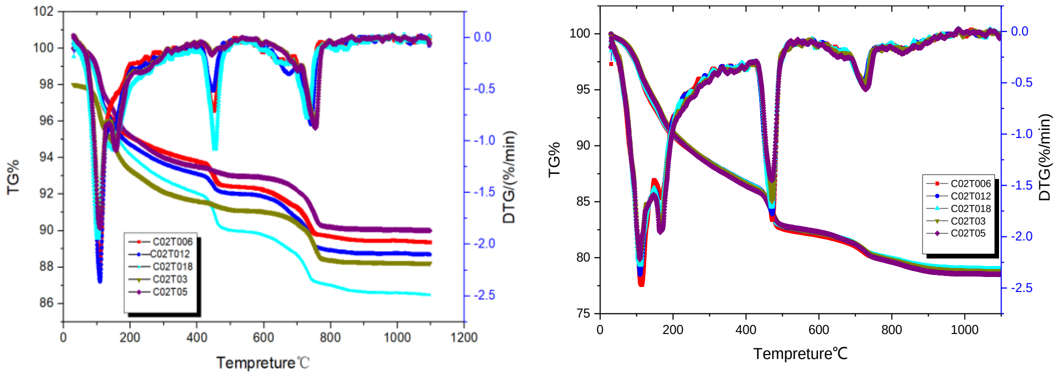
3.4 TG

According to the TG curve, the mass loss in the corresponding temperature range is defined as the dehydroxylation reaction (Ldx), dehydration (Ldh) and decarbonisation (Ldc), and the corresponding temperature range is listed in Table 4[11-13]. According to formula (1) and formula (2), the hydration degree of each sample can be calculated, and the results are listed in Table 4.

$$W_B = Ldh + Ld\mathrm{x} + 0.41(Ldc) \tag{1}$$

$$\alpha = \frac{W_B}{0.24} \times 100 \tag{2}$$

Where WB is the total amount of chemical bound water; 0.41 is the conversion of bound water in calcium hydroxide[13]; α is the degree of hydration of the sample; and 0.24 is the maximum amount of bound water required for cement hydration, generally 0.23-0.25[14,15].



(a) 3days **(b) 28days**

Figure 4: The TG curve of CA with different TEA dosages

Table 3: The chemically bound water and the degree of hydration

	Sample	Ldh % (70-400℃)	Ldx% （400-580℃)	Ldc% （580-1000℃)	WB	a %
3days	C002T006	5.85	1.49	2.85	8.51	35.46
	C002T012	6.60	1.17	3.19	9.07	37.81
	C002T018	7.49	2.19	3.27	11.01	45.90
	C002T03	6.18	0.55	2.84	18.18	32.87
	C002T05	6.31	0.56	2.90	8.05	33.54
28days	C002T006	12.21	4.63	3.34	18.20	75.85
	C002T012	12.21	4.51	3.24	18.04	75.18
	C002T018	12.24	4.38	3.29	17.97	74.87
	C002T03	12.49	4.25	3.49	18.18	75.74
	C002T05	12.66	3.98	3.84	18.22	75.91

The total amount of chemically bound water and the degree of hydration of the sample are shown in Table 3. As shown in table 3, with the TEA dosage increase, the hydration degree of the cement paste showed a trend of first increase and then decrease as the compressive strength in the early age, the hydration degree of C02T018 was up to 45.9%. Ultimately, by 28 days of hydration, all samples have a the same degree of hydration. it indicated that TEA and CA has a greater effect on the early hydration of cement, and a smaller effect on the later stage.

4. CONCLUSIONS

The effects of different amounts of TEA and CA on the hydration dynamics and mechanical properties of silicate cement were investigated. The results as follows:

Proper amount of TEA can offset the delayed effect of CA on hydration. When the TEA dosage is 0.18%, the setting time is lightly delay compare to OPC sample, and the compressive strength is similar to the same age OPC sample.

The total amount of chemical bound water and the degree of hydration of the sample results show that TEA and CA has a greater effect on the early hydration of cement, and a smaller effect on the later stage.

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