



Mechanism of triethanolamine on Portland cement hydration process and microstructure characteristics



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HIGHLIGHTS

- TEA accelerates hydration of C₃A, promoting hydration heat release rate.
- When TEA introduced, after depletion of calcium sulfate, AFt is converted to AFm.
- TEA retards hydration of C₃S, which can jeopardize concrete strength at early age.
- Influence of TEA on cement paste pore structure is dosage dependent.
- Balance should be made when using TEA, on its accelerating and retarding effect.

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ABSTRACT

Influence of triethanolamine (TEA) on Portland cement hydration heat evolution process, hydration product, pore structure, setting time and concrete strength were investigated; and mechanism of TEA on the cement hydration process and microstructure is discussed. Research results indicate that TEA accelerates hydration process of C₃A and retards that of C₃S, such effects enhance with the increase of TEA dosage. TEA also promotes rate of AFt formation and its conversion to AFm. As a result, TEA accelerates setting of cement paste but jeopardizes strength of concrete. Depending on its dosage, TEA can either optimize or harm cement paste pore structure. The types of calcium sulfoaluminate hydrate (AFt or AFm) produced in cement paste containing TEA depends on the abundance of calcium sulfate, before depletion of calcium sulfate, AFt is produced, after that, AFm is produced (converted from AFt).

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1. Introduction

Triethanolamine (TEA) is a weak base surfactant. It can be used as grinding aid for cement manufacturing (typically at dosage of 0.1%, weight percentage of clinker), in order to prevent agglomeration of powder and coating formation on milling ball surface [1]. TEA can also be used as component of chemical admixture, such as shotcrete accelerator or water reducing admixture, in order to accelerate cement setting or counteract the retarding effect of other component [2,3]. Previous research indicates that: (1) effect of TEA on cement hydration is objective oriented: it accelerates hydration process of C₃A but retard that of C₃S [4]. Ramachandran conducted a series of studies to investigate the influences of TEA on hydration process of C₃A, C₃A–gypsum and

C₃S and found that TEA accelerates C₃A hydration and C₃A–gypsum reaction by promoting formation of aluminate hydrate and AFt, and retards hydration process of C₃S by extending the induction period [5–7]; (2) effect of TEA on cement hydration is dosage dependent also. At small dosage (e.g. 0.02%, weight percentage of cement) it acts as setting accelerator, at higher dosage (e.g. 0.5%) it acts as setting retarder, at more higher dosage (e.g. 1.0%) it acts as setting accelerator once again [8].

Despite all the work have been done, the influence of TEA, especially at high dosage (higher than 1.0%), on Portland cement setting behavior and strength development still need further research, and the working mechanism of TEA on Portland cement hydration process and microstructure characteristics merit further investigation. Such research can facilitate TEA application and understanding of its effect in Portland cement manufacturing and utilization.

In this paper, TEA dosage from 0.02% to 8% was adopted, and its influence on Portland cement hydration process, hydration

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products, setting time, pore structure and concrete strength were studied.

2. Materials and mix proportions

Materials used include: type I Portland cement with chemical composition and fineness shown in Table 1; deionized water with resistivity no less than 10.0 MΩ cm; River sand with fineness modulus of 3.1; limestone with particle size ranging from 5 to 10 mm; polycarboxylate-based water reducing admixture (WRA); TEA was a liquid chemical reagent.

Cement paste mix proportion and properties measured are shown in Table 2. Concrete mix proportion is shown in Table 3, and 100 mm cubes are used for compressive strength evaluation.

3. Testing methods

Hydration heat evolution process of cement pastes was monitored by a differential scanning calorimeter (DSC) (ToniCAL, manufactured by Toni Company), under constant temperature of 25 °C.

The preparation of cement pastes for microstructure investigation consists of following steps:

- (1) Conducting a complete DSC test (0–24 h) for a cement paste.
- (2) Selecting a few key time points on the DSC curve so as to capture features of the hydration process of the paste.
- (3) Performing a series of DSC tests as described in Step (1) for the same cement paste; but, when the test reaches each of the key time points as described in Step (2), took the cement paste sample out of the DSC instrument chamber.
- (4) Cracking the samples into small pieces and submerging these small pieces into ethanol so as to discontinue the hydration process (It took less than 2 min from taking the sample out of the DSC instrument chamber to submerging the cracked pieces into ethanol; the volume ratio of ethanol to cracked pieces was about 10:1).
- (5) Studying the microstructure (hydration product and pore structure) of the cement paste.

Cement paste samples were taken out of ethanol and oven dried at 60 °C for 6 h. The oven dry process was to evaporate ethanol in capillary pore; then, pulverized using an agate pestle and mortar and passed through an 80 μm sieve, if powder was needed for measurement.

Hydration products of the above cement pastes were identified by X-ray diffractometer (Automated D/max, Rigaku Corporation), with a Cu Kα source and a scanning speed of 2° per minute.

TG–DSC–MS hyphenated method was used to verify the hydration product further. Using the TG–DSC instrument (STA 449 F3, Netzsch Company), under a controlled regime (from 50 to 1100 °C, heating rate of 20 °C/min; air atmosphere), the mass change and the difference of energy input between cement paste and reference material were measured simultaneously. Meanwhile, the gas released during TG–DSC testing process was transported to the MS instrument (QMS 403C, Netzsch Company) via capillary tube, and the input gas was ionized first and then classified and identified based on mass to charge ratio.

Pore structure of the paste samples was measured by BET absorption method. Cement paste samples were vacuum

Table 2
Cement paste mix proportion and properties measured.

Water to cement ratio (weight percentage)	Dosage of TEA [*] (weight percentage of cement) (%)	Properties measured
0.4	0, 0.02, 0.2, 2 and 6	Hydration heat evolution process
0.4	0, 0.2 and 6	Microstructure (including: hydration product and pore structure)
0.4	0, 2, 4, 6 and 8	Setting time

^{*} No water was deducted when TEA was introduced.

Table 3
Concrete mix proportion.

No.	Cement (kg/m ³)	Water (kg/m ³)	W/C	Sand (kg/m ³)	Aggregate (kg/m ³)	WRA (%)	TEA ^{**} (%)
C-TEA-0	490	196	0.4	830	880	1.5	0
C-TEA-5	490	196	0.4	830	880	1.5	5

^{**} Weight percentage of cement, and no water was deducted when TEA was introduced.

de-aerated for 6 h at 100 °C before measurement. Nitrogen (N₂) gas was used as adsorbate. Measurement was performed by a surface area and pore analyzer (Quadrasorb SI, Quantachrome Company). Pore volume and pore size were calculated based on the amount of N₂ adsorbed.

Setting time of cement pastes with different dosages of TEA was measured according to ASTM C191 by Vicat apparatus, under temperature of 23 ± 2 °C. Compressive strength of concrete was measured at 1 day of age according to ASTM C39.

4. Results and analysis

4.1. Effect of TEA on hydration heat evolution process

During Portland cement hydration process monitored by DSC method, there are usually 5 stages: (A) initial reaction period, (B) induction period, (C) acceleration period, (D) deceleration period, and (E) slow reaction period [9]. There are usually two peaks during the hydration process, the first peak, in initial reaction period, is mainly resulted from ion dissolution and reaction between C₃A and calcium sulfate, usually resulting in formation of AFt; the second peak, at the end of acceleration period, is mainly resulted from hydration of C₃S, forming C–S–H and calcium hydroxide (CH) [10].

Hydration heat release rate curves of cement pastes with different dosage of TEA are given in Fig. 1. It can be seen in the figure, as the TEA dosage increases, the hydration heat release rate in initial reaction period is promoted, the induction period is prolonged, and the acceleration period is postponed. When TEA dosage is higher than 2%, no acceleration period can be identified during the 24 h measurement. An affiliated peak is noted right after the main peak in the initial reaction period, which corresponds to the conversion of AFt to AFm as explained by XRD measurement in later part of this paper.

The promoted hydration heat release rate in initial reaction period is due to the accelerating effect of TEA on reaction of C₃A with calcium sulfate. TEA can chelate with some cation ions, such as Al³⁺, Fe³⁺ and Ca²⁺, under highly alkaline medium [11,12]. When chelated with Al³⁺, TEA can promote formation of calcium sulfoaluminate hydrate (AFt and AFm) and accelerate hydration process of C₃A.

The postponed hydration process of C₃S after the introduction of TEA might be attributed to TEA's chelating ability with Fe³⁺ and Ca²⁺ cations. Due to mineral structure characteristics, the

Table 1
Chemical composition and fineness of Portland cement.

Oxide (wt.%)								Blaine fineness (m ² /kg)
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O _{eq}	F-CaO	
21.58	4.03	3.46	61.49	2.60	2.83	0.51	0.67	346
C ₃ S		C ₂ S		C ₃ A		C ₄ AF		LOI (wt.%)
57.34		18.90		6.47		11.25		1.97

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