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Influence of triethanolamine on the hydration product of portlandite in cement paste and the mechanism

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ABSTRACT

The influences of triethanolamine (TEA) on the portlandite in hardened cement pastes (HCPs) were systematically investigated. Results show that the addition of TEA in cement pastes leads to a visible reduction of Ca$(OH)_2$ (CH) content and considerably alters the morphology of CH crystals from large and parallel-stacked lamellar shape to smaller and distorted actinomorphic one. For the first time, the CH micro-crystals and even non-crystalline CH in HCPs were observed in the presence of TEA. Due to integration of CH micro-crystals in C–S–H phase, remarkable higher Ca/Si ratio of C–S–H phase was found. The formation of TEA-Ca^{2+} complex via the interaction between Ca^{2+} and the oxygen atoms in TEA molecule was evidenced by the results of NMR and UV. It is believed that TEA can be introduced into the crystallization process of portlandite and thus significantly alters the morphology of CH crystals and even the content of the crystalline CH phase.

1. Introduction

Triethanolamine (TEA) has been popularly used as one of the components of grinding aids for Portland cement and sometimes been used as an accelerator for concrete in the past decades. The main function of TEA in grinding aids is to facilitate the grinding process of the clinker by modifying the surface feature of clinker particles [1]. When TEA is used as an accelerator in concrete or mortar, it is expected to promote the setting and the strength development of cementitious materials. It is well known that the behavior of TEA in cementitious system is highly dependent on the dosage. TEA acts as a set accelerator at low dosages (e.g. 0.02%–0.05% by weight of cement, bwoc) and evidently enhances the early strength of cementitious materials [2], 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 [3].

In order to understand the surprising effects of TEA in cementitious materials, extensive research on the working mechanism of TEA has been carried out in the context of investigating the impacts of TEA on the kinetics of cement hydration and the microstructure of hydration products. Ramachandran [4,5] found that 0.1% dosage of TEA retarded the hydration of C_3S by extending the induction period but accelerated the hydration of C_3A. And he deduced that the adsorption of the amine-containing cation on the freshly formed C–S–H surface led to the prolonged induction period whereas the formation of a complex of TEA with the hexagonal aluminate hydrate on C_3A surface might be responsible for the accelerated hydration of C_3A. Gartner and Myers [6] reported that TEA increased the dissolution of iron containing phase at dosage of 0.24% and proposed that tertiary alkanolamines acted as 'diffusion facilitators' for ferric ions and thus increased the hydration degree for C_4AF. Cheung et al. [7] pointed out that an increase in dissolution of iron contributed little to the enhanced strength at TEA dosage of less than 0.03%. As regard to the hydration products, ettringite (AFt) crystals with smaller size were observed when 0.1% TEA was added in cement pastes [8]. Ramachandran [5] proposed that the addition of TEA (0.1%–1.0%) in hydrating C_3S promoted the formation of C–S–H with a higher Ca to Si ratio (Ca/Si). Moreover, he inferred that non-crystalline $Ca(OH)_2$ might be formed in the presence of TEA on the basis of TGA and XRD results. The hydration product of portlandite phase, which is usually parallel-stacked lamellar crystals with dimension of tens of micrometers and accounts for 20–25% of hydration products in HCPs, is often considered as the weakest part in hardened cement pastes (HCPs), responsible for the micro-crack initiation and growth [1]. The variation in content and morphology of the portlandite is believed to play a key role in the setting and strength development of HCPs. However, so far, no direct experimental evidence on morphological changes of portlandite in the presence of TEA has been reported in literatures.

In spite of much effort put on the influences of TEA on cement hydration and microstructure of HCPs, the explicit effects of TEA on portlandite phase as well as its working mechanism have not been

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Table 1
Chemical and mineralogical composition of cement (wt/%).

Chemical composition								Mineralogical composition			
CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O	C_3S	C_2S	C_3A	C_4AF
59.79	22.43	4.46	3.94	3.80	3.68	0.99	0.16	26.40	44.47	5.16	11.98

Table 2
Particle size distribution of the cement.

Particle size	<3 μm	3–32 μm	32–65 μm	>65 μm
Volume distribution (%)	10.43	59.98	29.17	0.45

fully disclosed. In this study, the changes on the morphology of CH phase and its content in hardened cement paste in the presence of TEA were systematically investigated by means of non-evaporable water (NEW), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Pore solution analysis of hydrating cement pastes, ultraviolet–visible (UV/Vis) spectrophotometry and nuclear magnetic resonance (NMR) spectroscopy were conducted with the aim of elucidating the working mechanism of TEA from a chemical point of view. To disclose the effects of TEA on the portlandite phase in HCP may bring a new insight of understanding the impacts of TEA on cement hydration and the strength development of HCP.

2. Experimental

2.1. Materials

Portland cement was prepared by grinding a clinker together with 5% gypsum in a laboratory ball mill, whose chemical composition, mineralogical composition and particle size distribution are respectively shown in Table 1 and Table 2. The composition of the cement was obtained by X-ray fluorescence analysis and the particle size distribution was measured by using the laser particle size analyzer. Analytical grade of chemicals including triethanolamine (TEA), $CaCl_2$, KOH and $Ca(OH)_2$ were used as received (all >98% purity). Deionized water was used in all experiments in this study including the preparation of cement pastes.

2.2. Paste experiments

Measurements of hydration degree and microstructural characterization were carried out on cement pastes which were prepared with a fixed water to cement mass ratio of 0.32 to minimize any bleeding effects. The dosages of TEA by weight of cement were set at 0%, 0.03%, 0.1%, and 1.0%. TEA was firstly dissolved in water and then well mixed with cement in a 2.5 L stirring mixer for about 5 min at 125 rpm. After well mixed, the fresh cement paste was cast and sealed in steel mold with the dimension of 200 mm × 200 mm × 200 mm for curing in a standard curing room (moist curing at 20 °C and 95% relative humidity (R.H.)). At the selected ages, the specimen was broken into small pieces (<10 mm) and a piece of sample from the center part of the specimen was selected. It was immediately moved into an ethanol bath and then stored for at least 24 h to terminate cement hydration. Thereafter, it was grounded to powder in ethanol and dried in a vacuum drying oven at 65 °C for 24 h. Finally, the following measurements of cement hydration were carried out.

2.2.1. Cement hydration

In order to determine the effects of TEA on cement hydration with emphasis of the content of CH in hardened cement pastes (HCPs), the measurements of non-evaporable water (NEW), TGA and XRD were conducted using the ground HCP powder.

NEW content is a useful indicator of the hydration degree of cement and a larger NEW content generally suggests a higher hydration degree [9]. In the measurement of NEW content, the pulverized HCP samples were stored at 105 °C to remove the evaporable water until their weight remained unchanged. After that, the samples were dehydrated at 1000 °C until their weight remained unchanged. The mass loss in the

Table 3
^{1}H-NMR analysis of TEA in different solutions.

Test no.	Solutes in D_2O solutions	Concentration of solutes (mmol/L)	pH	δ_1/ppm	δ_2/ppm	$\Delta\delta$/ppm
A0	TEA	20	10.92	3.544	2.599	0.945
A1	TEA and $Ca(OH)_2$	TEA: 20, $Ca(OH)_2$: 20	13.29	3.545	2.584	0.961
B1	TEA and KOH	TEA: 20, KOH:40	13.37	3.532	2.585	0.947
C1	TEA and $CaCl_2$	TEA: 20, $CaCl_2$: 20	10.90	3.566	2.606	0.960

Note: Only the main peaks of the chemical shifts are listed in this table (δ_1, δ_2), because of the split of the peaks.

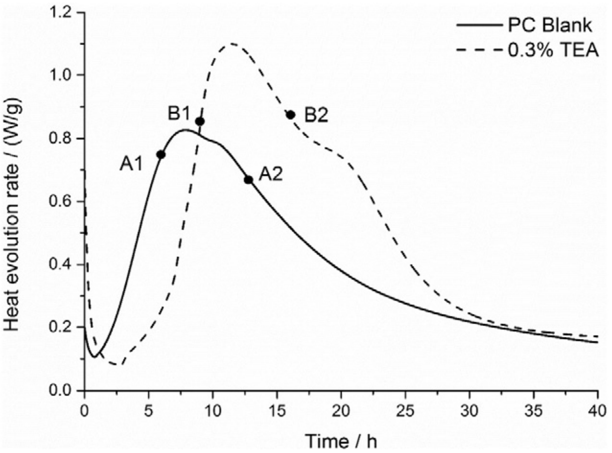

Fig. 1. Heat evolution curves of the hydrating cement pastes in the absence and the presence of TEA.

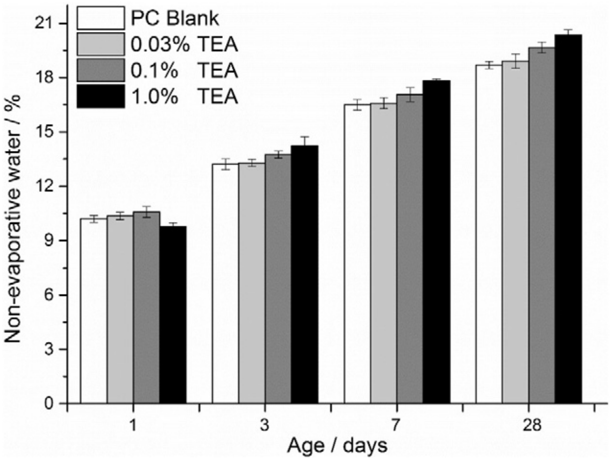

Fig. 2. Effects of TEA on the content of non-evaporable water of the hardened cement pastes.