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.

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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$_3$S by extending the induction period but accelerated the hydration of C$_3$A. 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$_3$A surface might be responsible for the accelerated hydration of C$_3$A. 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$_4$AF. 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$_3$S 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.
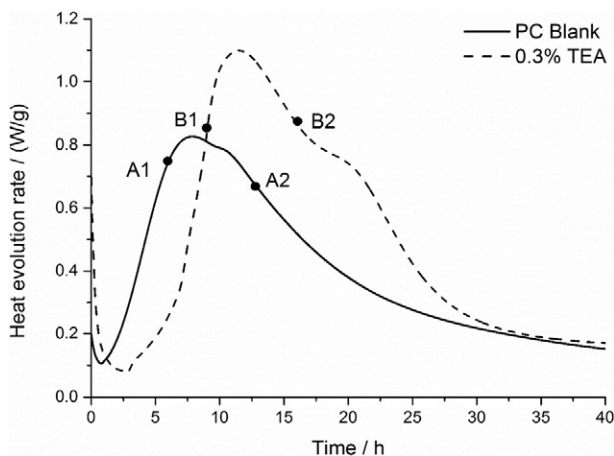

Fig. 1. Heat evolution curves of the hydrating cement pastes in the absence and the presence of TEA.
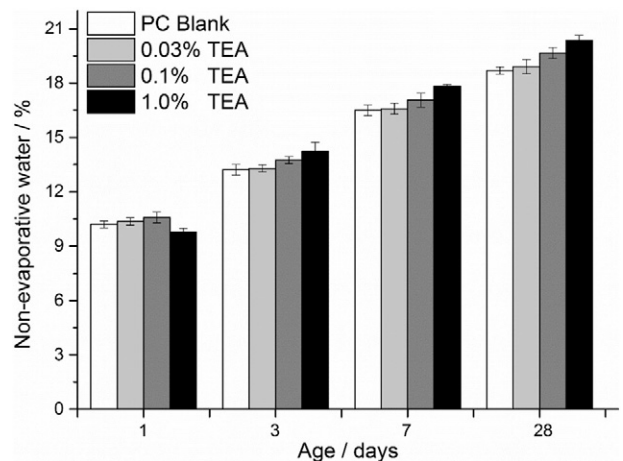

Fig. 2. Effects of TEA on the content of non-evaporable water of the hardened cement pastes.

temperature range of 105 °C to 1000 °C was defined as the content of NEW.

TGA is one of the most accurate method for analyzing the CH content in HCPs. TGA measurements (DTG-60H, Shimadzu, Japan) were performed by heating the HCP samples from 50 °C to 850 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The CH content was obtained by determining the mass loss in the temperature range of 400–500 °C using the tangent method.

XRD is usually used to semi-quantitatively analyze the content of crystallized CH in hardened cementitious materials. FT scanning was carried out on the HCP samples at a 2θ range of 17–19° where the diffraction peak of typical CH crystal locates using an X-ray diffractometer (Rigaku D/max 2550, Japan). The step length was 0.02° and the settle time of every step was 6 s. The integrated intensity of the diffraction peak of CH was calculated, which is proportional to the CH amount.

2.2.2. Morphology of hydration products

Scanning electron microscopy (SEM) and transmission electron microscope (TEM) were used to directly observe the microscopic morphology of hydration products in the HCPs.
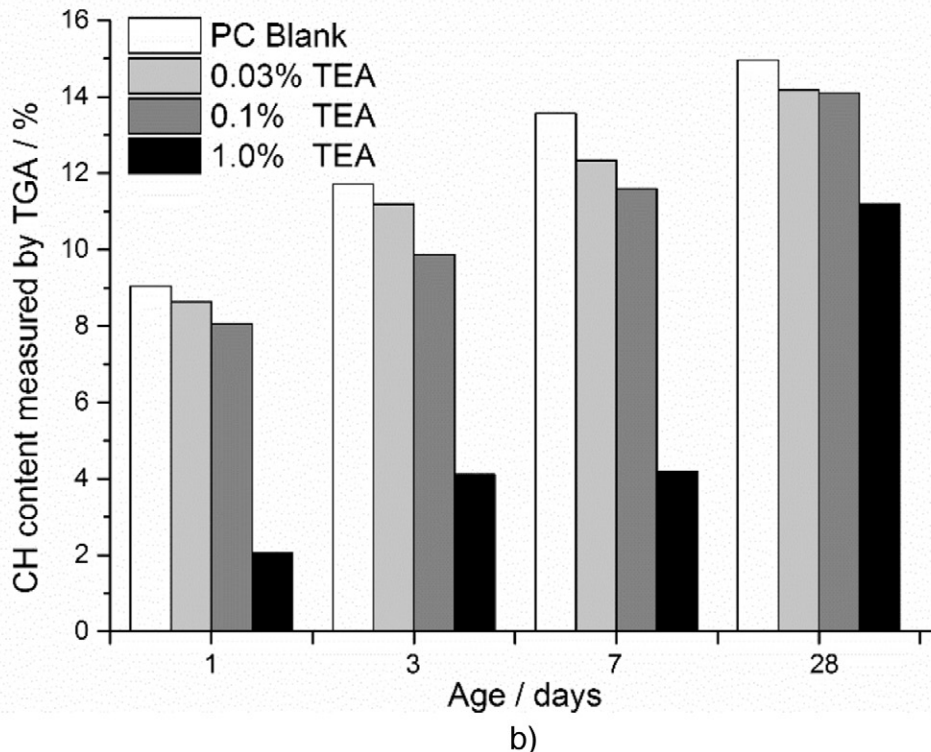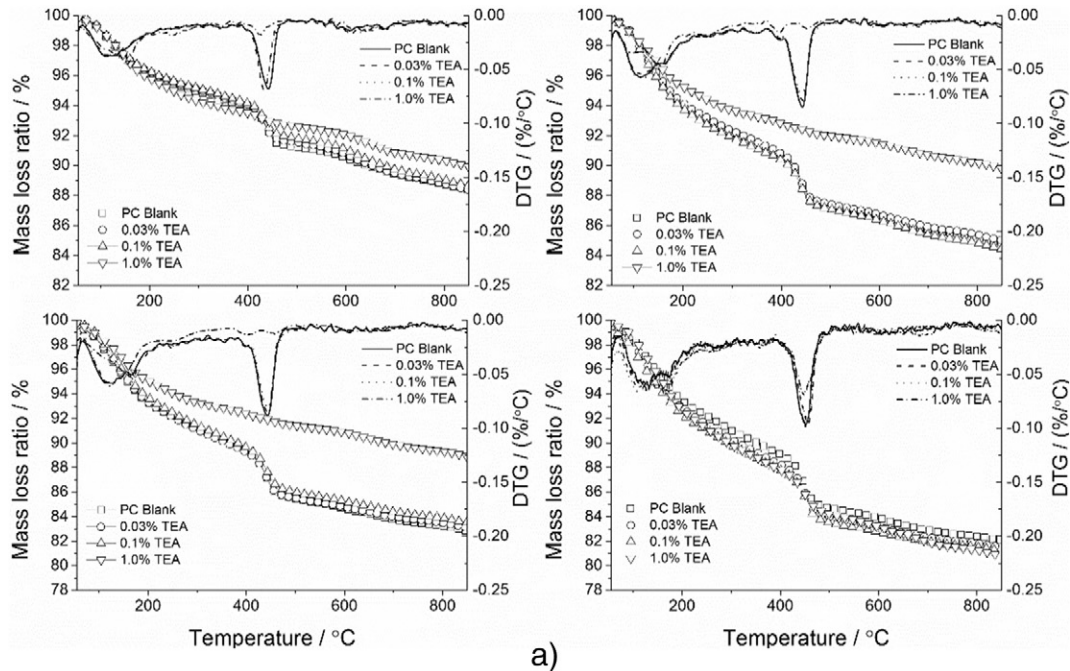

Fig. 3. TGA-DTG data of hardened cement paste at different ages (a) and the amount of Ca(OH)$_2$ in cement pastes determined by TGA (b) [1].
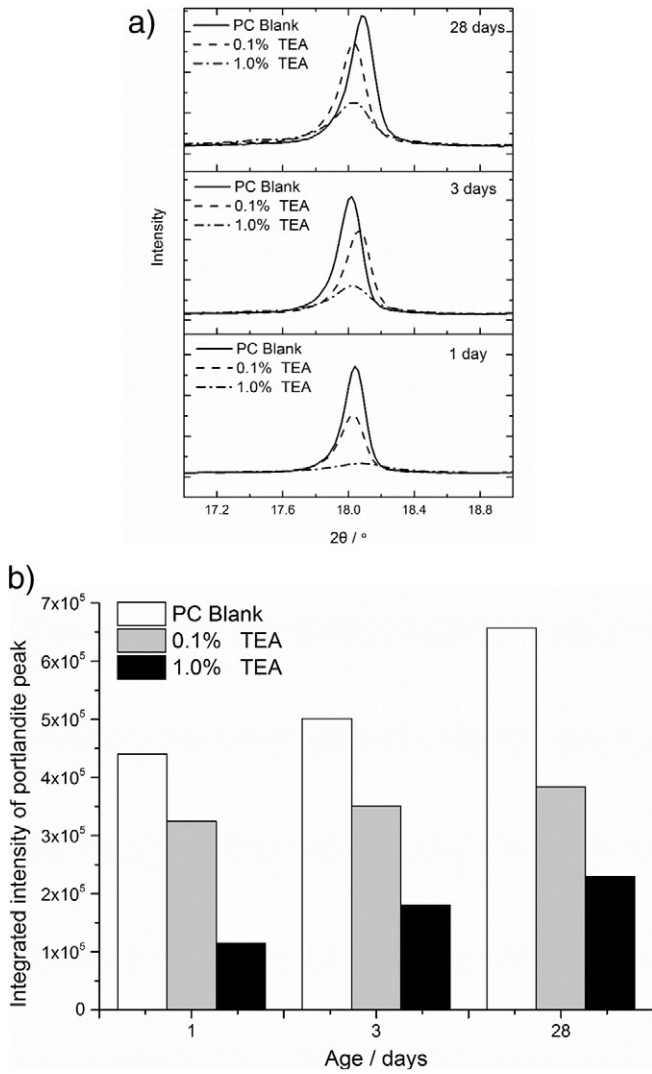
Fig. 4. The XRD curves of hardened cement pastes at different ages (a) and the amount of Ca(OH)$_2$ in cement pastes determined by XRD (b) [1].

HCP cubic samples without and with TEA cured at ages of 1, 3 and 28 days respectively were subjected to SEM measurement. In order to ensure the influence of TEA on the microstructure of the hydration products could be clearly observed from a micrometer scale even at early ages, i.e. 1 and 3 days, a high TEA dosage of 1.0% was chosen and the W/C was fixed at 0.32. After cured for 1, 3 and 28 days, the HCP samples were broken into small pieces with dimension of about 5 mm and then moved into an ethanol bath and stored for at least 24 h to terminate cement hydration. Thereafter, they were dried in a vacuum drying oven at 65 °C for 24 h. Subsequently, a freshly prepared section surface of the HCP was sputtered with a carbon layer. SEM imaging was performed using SEM (QUANTA 200FEG) under high vacuum with the voltage 15 kV.

Field emission gun scanning transmission electron microscope (FEG-STEM) (Tecnai G2 F20–200 kV) allows a direct observation on the morphology of the hydration products with a higher resolution than SEM. An equipped energy dispersive X-ray (EDX) spectroscopy in the TEM enables a direct analysis on the elemental composition of the selected phases observed by TEM, and the crystal type of these phases could be further analyzed by the selected area electron diffraction (SAED) technique at the meantime.

The hydration products in the blank cement paste and the paste containing 0.3% TEA were analyzed by TEM at time points of before and after the maximum exothermic peak in the hydration heat curves which could be obtained by the isothermal calorimetry tests. Prior to TEM experiments, TAM-air micro-calorimeter (Thermometric AB, Sweden) was employed to monitor the heat evolution of the blank HCP and the HCP at TEA dosage of 0.3% and W/C of 0.32. Before tests, the calorimeter was regulated at a constant temperature of 25 ± 0.02 °C and then equilibrated for 24 h. Thereafter, the freshly mixed samples containing 6.776 g of cement were promptly decanted to an ampoule of 20 mL and then placed into the channels. The heat evolution curve within 72 h was recorded and shown in Fig. 1. For the blank cement paste, the maximum exothermic peak appears at the time point of 8 h after cement to water contact, while the peak emerges at about 13 h for the cement paste with 0.3% TEA. Thus, TEM measurements were conducted on the blank cement paste at 6 h (A1 age) and 13 h (A2 age) and on the paste containing TEA at 9 h (B1 age) and 16 h (B2 age), which ensures that the hydration products in the blank paste and the one containing TEA were produced in a similar hydration stage before and after the peak.

At the selected time, the cement paste was diluted to a solid content of 1% by adding ethanol and dispersed by ultrasonic oscillation for 10 min. The cement suspension was then dropped on a copper mesh and was subjected to the TEM observation after the sample was completely dried out.

2.2.3. Pore solution analysis of hydrating cement pastes

In the pore solution of the hydrating cement paste, the concentration of TEA was measured by a total organic carbon (TOC) analyzer (Shimadzu, TOC-VCPH, Japan) and the concentration evolution of various elements including Na, K, Ca, Fe, Al, S, Si and pH with hydration time was monitored by a inductively coupled plasma optical emission spectrometry (ICP-OES) (IRIS Intrepid II XSP, Thermo Fisher, USA).

Two TEA solutions with the concentrations of 19 and 190 mmol/L were respectively prepared. The former one was used to mimic the initial TEA concentration in the paste with W/C of 0.32 and TEA dosage of 0.1% while the later one attempted to amplify the influence of TEA on the elemental concentrations in pore solution for easy detecting. The cement paste sample was prepared by mixing cement powder with the TEA solutions. In order to obtain sufficient pore solution from the hydrating cement pastes, the W/C of cement pastes was heightened to 0.6. The mixture was then slowly agitated in a sealed polyethylene flask by using a head-over laboratory agitator to keep the homogeneity. At the selected time points (5 min, 30 min, 1 h, 4 h, and 8 h), a portion of the fresh cement paste was taken out and immediately centrifuged at 3000 rpm for 10 min. Clear supernatant solution was then collected by using a syringe filter with pore diameter of 0.22 μm and was subjected to the measurements of TEA concentration and the element concentrations.
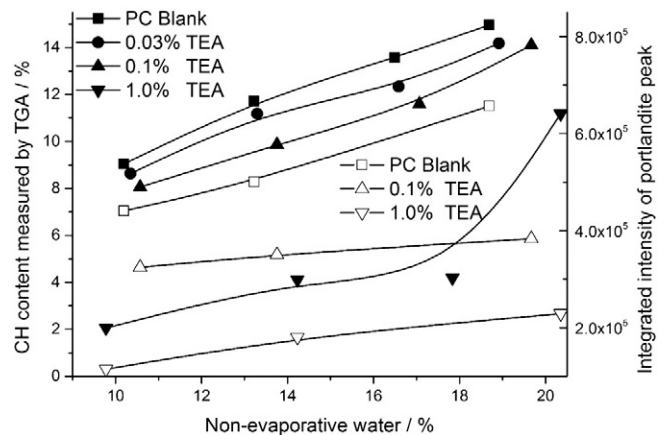

Fig. 5. The CH content measured by TGA and XRD versus the content of non-evaporable water in cement pastes.
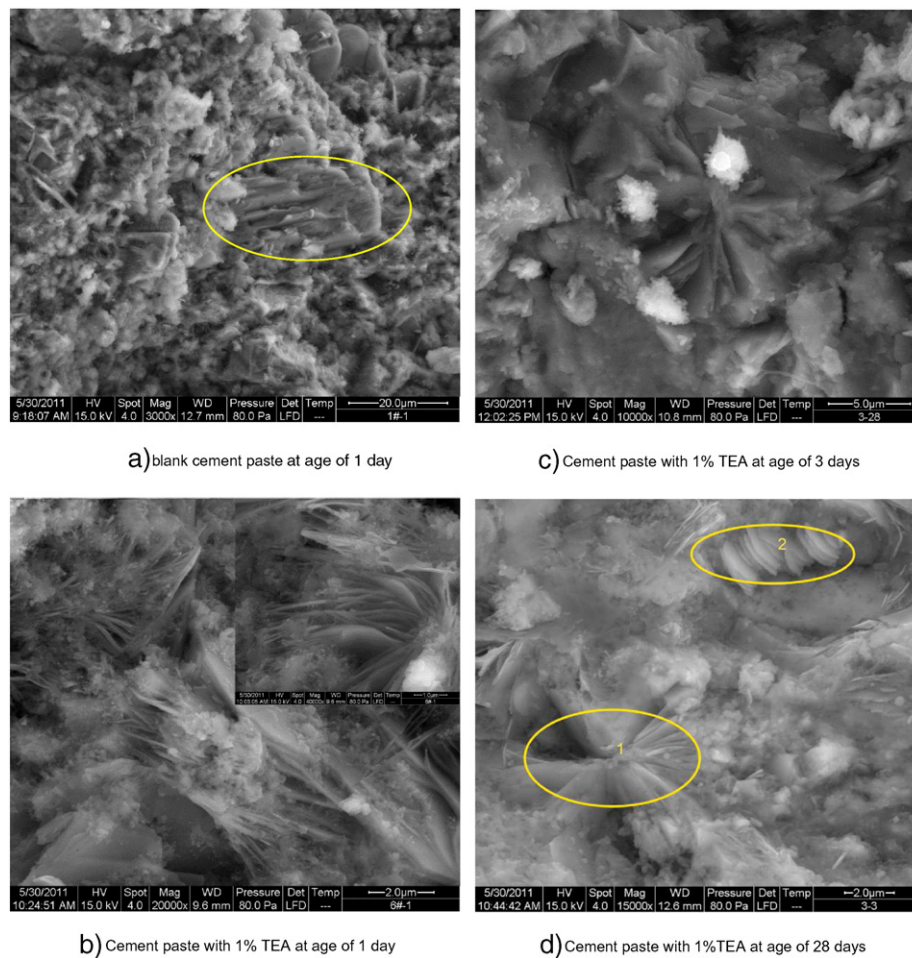
Fig. 6. Effect of TEA on the morphology of portlandite in cement pastes with and without addition of TEA at fixed W/C of 0.32 [1].

2.3. Solution experiments

To study the complexation effect between TEA and calcium ions, a systematic investigation on the saturated $Ca(OH)_2$ solutions with and without TEA was carried out by means of conductivity analysis, ^{1}H-NMR spectroscopy, and ultraviolet (UV) absorption spectroscopy.

The complexation effect between TEA and Ca^{2+} may bring about the changes on the conductivity and pH value of saturated $Ca(OH)_2$ solution in the presence of TEA. A conductivity meter (DDS-11A, Yoke, China) and a pH meter (FE-20K, Mettler Toledo, USA) were employed to measure the conductivity and the pH value of the saturated $Ca(OH)_2$ solutions in the presence of TEA at different concentrations. Firstly, a large amount of $Ca(OH)_2$ powder was added into deionized water and the suspension was subjected to intense agitation for 1 h to reach the dissolution equilibrium under sealed condition to avoid the reaction between CO_2 and $Ca(OH)_2$. The mixture was then stored for complete sedimentation and then clear saturated $Ca(OH)_2$ solution was obtained by syringe filtration. Different amounts of TEA were added to the above prepared clear saturated $Ca(OH)_2$ solutions and the mixtures were subjected to measurements of conductivity and pH value. For comparison, the conductivity and pH value of the corresponding saturated $Ca(OH)_2$ solutions with varied TEA concentrations in the presence of $Ca(OH)_2$ precipitate were also measured.

^{1}H-NMR spectroscopy serves as an accurate method for investigating the structure of organic complexes. A nuclear magnetic resonance spectrometer (JNM-ECA600, JEOL, Japan) was employed to study the change of the chemical shift of hydrogen atom in TEA molecule caused by the interaction of Ca^{2+} with TEA. The ^{1}H-NMR spectra of TEA in D_2O solution were recorded with the field strength of 600 MHz. When $Ca(OH)_2$, KOH, and $CaCl_2$ were introduced into the TEA solutions with D_2O as solvent, the same measurements were carried out respectively and the changes in chemical shift of hydrogen atom were recorded. The concentrations of solutes in the D_2O solution are given in Table 3.

Ultraviolet spectrophotometry can also be used to investigate complex structures by analyzing the absorption peaks in the UV spectrum. Different amounts of $Ca(OH)_2$ were respectively dissolved into a previously prepared TEA solution with concentration of 5 mmol/L. The UV spectra of the mixtures were recorded by a spectrophotometer (IU-3900, Hitachi, Japan) with a scanning wavelength of 200 to 600 nm.

3. Results and discussion

3.1. CH content in hydrating cement pastes

Usually, the CH content in a HCP is closely related to the degree of cement hydration and a higher CH content corresponds to a larger hydration degree. The influence of TEA on the hydration degree is determined by measurement of NEW content, as shown in Fig. 2. It is clearly seen that the NEW content in the HCPs at ages of older than 3 days progressively grows with the dosage of TEA, indicating that TEA accelerates the cement hydration. At age of 1 day, NEW content is less affected by TEA at lower dosage, and 1% addition of TEA even decreases the hydration degree.

As one of the main hydration products, the content of CH in HCP should be usually proportional to the hydration degree. Based on the result presented in Fig. 2, it is expected that the addition of TEA should

have increased the CH content in HCPs at ages of older than 3 days. However, from the results of TGA and XRD as indicated in Figs. 3–4, it is surprisingly found that the CH contents in all the HCPs at varied ages are obviously lowered by the addition of TEA, which is obviously contrary to the result of NEW content measurement.

In order to further analyze the effect of TEA on CH content, the CH contents measured by TGA and XRD are plotted in function of the NEW content, as shown in Fig. 5. It is interestingly noted at all tested ages the addition of TEA reduces the CH content compared to the blank cement paste. The XRD results indicate more reduction of CH content caused by the addition of TEA than the TGA measurements. This suggests that TEA may affect not only the content of CH in a hardened cement paste, but also the crystalline morphology of CH phase, because TGA measurement is based on the thermal decomposition of CH phase, while XRD measurement is effective only for the crystalline CH phase. This phenomenon has been reported by other researchers [5,6,10]. They found a decrease in the amount of portlandite in hydrated C_3S pastes treated with TEA at the same hydration degree and the reduction

was larger determined by XRD than that by TGA. They hypothesized that the decrease in CH content by the addition of TEA may originate from the formation of the non-crystalline CH or a higher Ca/Si ratio in C–S–H phase due to the integration of the CH micro-crystals in the C–S–H phase. However, straightforward experimental evidence has not yet been provided so far.

3.2. Morphology of hydration products

In order to prove the hypothesis and to provide a clearer interpretation to the effect of TEA on the formation of CH phase during cement hydration, techniques of SEM and TEM were employed for direct observation of the hydration products, especially the portlandite crystals.

3.2.1. SEM

SEM observations were carried out to compare the morphology of cement pastes with or without TEA at different ages. Fig. 6 shows the
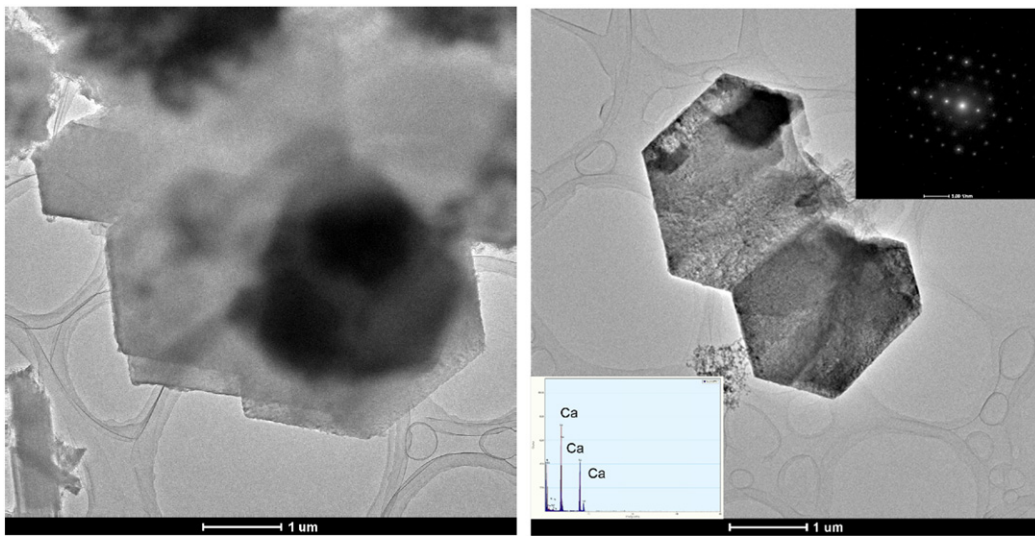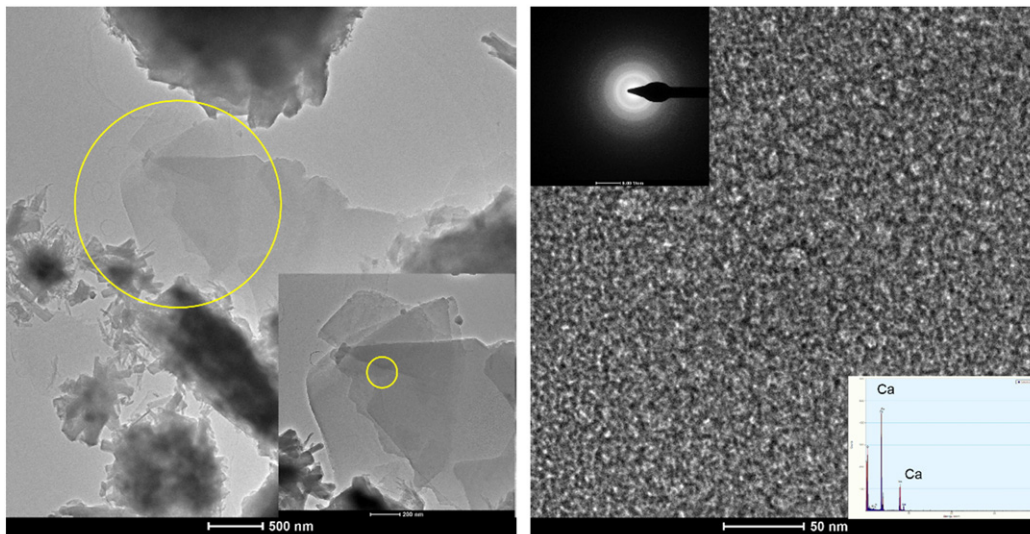

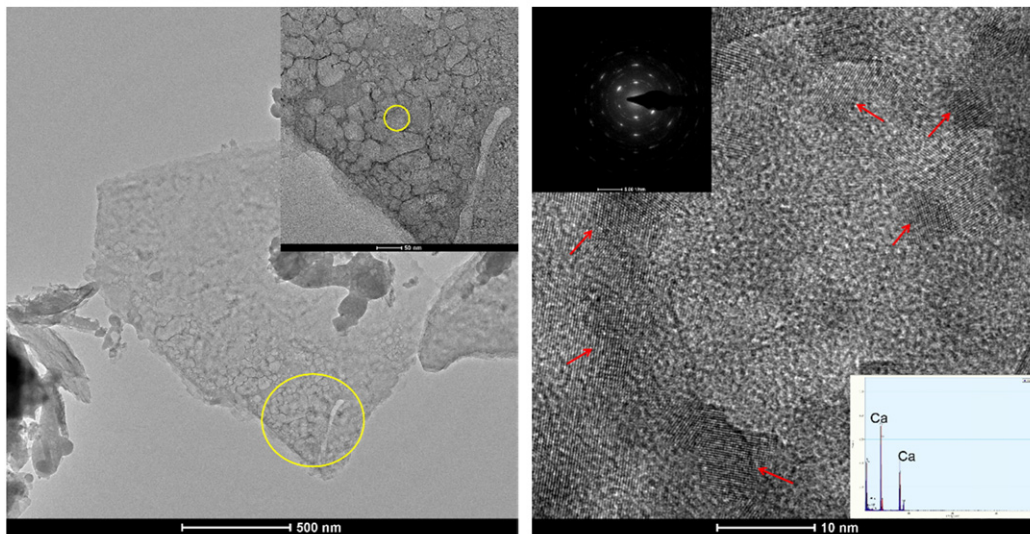(a) Blank cement paste at time point of A1 (6 h)
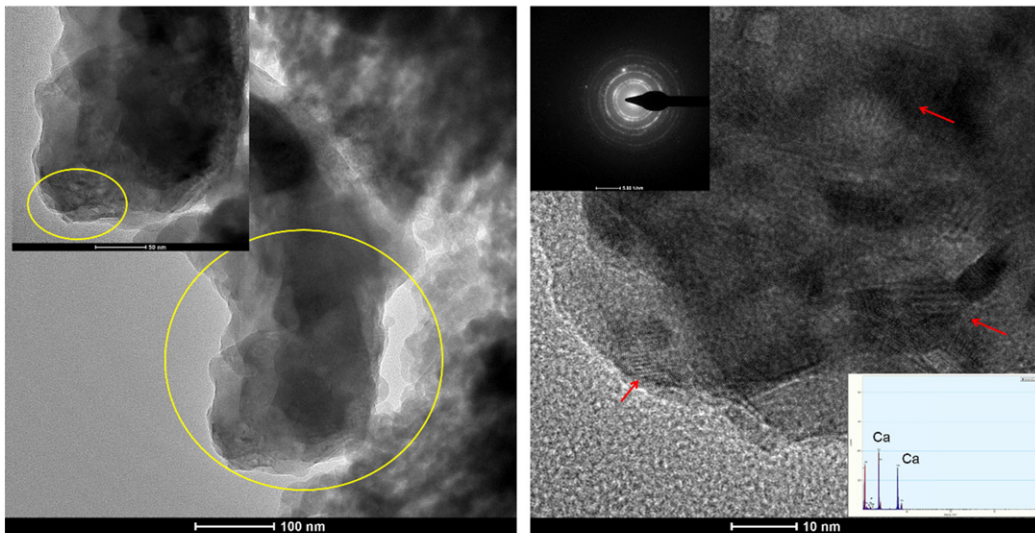
(b) Blank cement paste at time point of A2 (13 h)

Fig. 7. TEM images of the CH phase in hydrating cement pastes with EDX spectrum and SAED pattern inserted.

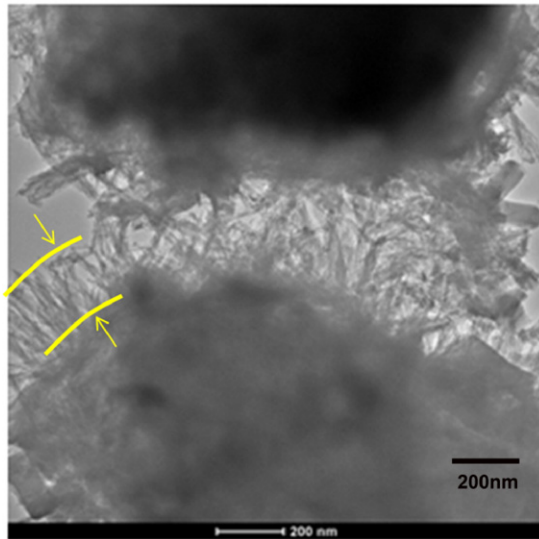(c) Cement pastes with 0.3%TEA at time point of B1 (9 h)

(d) Cement pastes with 0.3%TEA at time point of B2 (16 h)

Fig. 7 (*continued*).

SEM images of the blank HCPs at 1 and 28 days and the HCP with 1% TEA at 1, 3 and 28 days with emphasis of the portlandite phase. For the blank HCP without TEA, typical parallel-stacked lamellar CH crystals with large size of tens of microns are observed in Fig. 6(a). In comparison, with the addition of 1% TEA, the morphology of the CH is extremely altered, as shown in Fig. 6(b). Many CH crystals with much smaller size are present in the HCP and they arrange in a distorted, actinomorphic form. Fig. 6(c) and (d) show that at 3 and 28 days of age, large amounts of distorted CH crystals are still visible (Fig. 6(d), area 1), together with a minority of later formed CH crystals with parallel-stacked lamellar shape and with smaller size (Fig. 6(d), area 2). These lamellar CH crystals are supposed to be produced after the depletion of TEA molecules in pore solution. Due to the limitation of available space in hydrating cement pastes, the late-produced lamellar CH crystals are forced to be smaller in size. Thus, it is confirmed that the addition of TEA certainly leads to the morphological change of CH crystals from a larger and parallel-stacked lamellar form to a smaller and distorted actinomorphic one.

3.2.2. TEM

TEM equipped with an EDX spectroscopy and an inserted SAED function enables a direct observation on CH phase with a higher resolution and an accurate analysis on the elemental composition and crystal structure of the observed phase. The cement pastes with and without addition of 0.3% bwoc TEA were prepared with the fixed W/C of 0.32 for TEM imaging. As mentioned in Section 2.2.2, prior to TEM analysis, isothermal calorimetry measurements were performed to select the appropriate testing time points at which cement hydration is undergoing similar stage in different cement pastes. As indicated in Fig. 1, the hydrating cement pastes with and without addition of TEA were analyzed before and after the main hydration peak, namely at time points of A1, A2 for the blank cement paste and B1, B2 for the TEA containing cement paste respectively. Fig. 7 presents the TEM images of CH phase in the pastes with and without TEA at the selected ages (A1, A2, B1, B2). As shown in Fig. 7(a), the typical hexagonal sheet single crystal of CH is found in the blank cement paste, which is confirmed by the elemental composition and the ordered diffraction pattern. On the other hand, in

(a) Blank cement paste at time point of A1 (6 h)
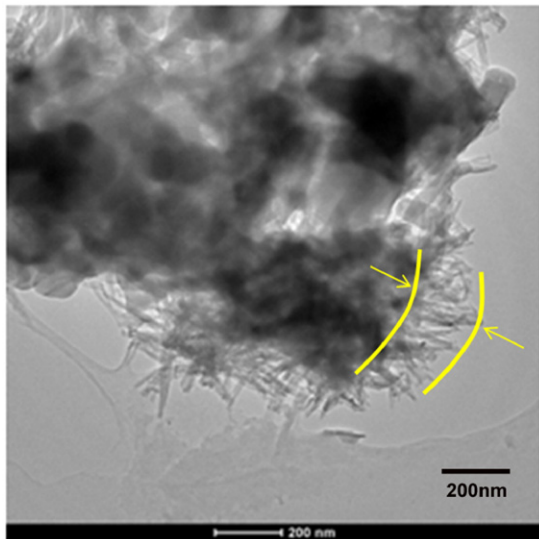
(b) Cement pastes with 0.3%TEA at time point of B1 (9 h)

Fig. 8. TEM images of the C–S–H phase in hydrating cement pastes in the absence (a) and the presence (b) of TEA.

the case of the cement paste containing TEA, some irregular sheet hydration products are found at the age of B1, which are identified as CH phase according to the elemental analysis. Unlike the typical diffraction pattern of the portlandite crystals, as seen in Fig. 7(c), the electron diffraction patterns are stretched and even deformed to a ring-like pattern, which suggest that the analyzed CH phase is amorphous or crystalline phase with lower regularity such as micro-crystals according to the Debye–Scherrer formula [11]. This result, for the first time, provides the direct evidence of the non-crystalline CH and CH micro-crystals originated from the addition of TEA in cement pastes. It is the formation of the CH micro-crystals or non-crystalline in hydration products that leads to a larger reduction in the CH content determined by XRD than that by TGA when TEA is added, because such CH phase may exhibit different thermal decomposition temperature in TGA measurement due to the incorporation of organic chemicals and may even not be able to be detected by XRD measurement.

With the progressing cement hydration, many smaller and irregular sheet CH are observed at age of B2 (Fig. 7(d)). The discontinuous

diffraction rings demonstrate that the CH is poly-crystals which consist of many CH micro-crystals or hexagonal CH crystals particles with different orientations. This is in consistent with the observed SEM images of the distorted actinomorphic CH crystals.

With regard to the C–S–H phase, the addition of TEA does not notably change the morphology of C–S–H gel and the growth thicknesses of C–S–H are almost equivalent at the similar hydration stage regardless of the addition of TEA (Fig. 8). However, the Ca/Si ratio of the C–S–H is dramatically increased on the basis of the elemental analysis on the observed C–S–H in different locations, as presented in Fig. 9. For the blank cement paste, the Ca/Si ratio mostly locates in the range of 1.0–2.0 and the average Ca/Si ratio is about 1.60, which is fairly consistent with the literatures [12,13]. In the case of the cement paste with TEA, the EDX analysis of the C–S–H composition of more than 40 points demonstrates a higher Ca/Si ratio (the average Ca/Si ratio = 2.02) caused by the addition of TEA. In many locations of the C–S–H phase, the local Ca/Si ratio reaches as high as 3.0–4.0. This is again in good agreement with the findings in the literature that the addition of TEA leads to a higher Ca/Si ratio of C–S–H [5]. Based on the abovementioned findings of the effects of TEA on morphology of CH phase, it is reasonable to ascribe the higher Ca/Si ratio to the incorporation of CH micro-crystals in C–S–H phase, which was supposed by Riding et al. [10] for the other alkanolamine (DEIPA).

From the discussion above, it is confirmed that the addition of TEA exerts notable influences on the content as well as the morphology of CH phase. The CH content is dramatically reduced by the addition of TEA, which is a consequence of the formation of the CH micro-crystals or non-crystalline CH and a higher Ca/Si ratio in C–S–H phase. In the presence of TEA, the morphology of CH crystals changes from larger and parallel-stacked lamellar shape to smaller and distorted actinomorphic one. For the first time, it is proved that the CH micro-crystals and even non-crystalline CH in HCPs are produced in the presence of TEA by means of TEM and SAED. Furthermore, when the CH micro-crystals are embedded in C–S–H phase, the Ca/Si ratio of C–S–H phase increases.

3.3. Pore solution analysis

Pore solution analysis of the fresh cement pastes in the presence and absence of TEA was conducted to provide more insight of the mechanism behind the influences of TEA on morphology of hydration products, especially on the morphology of CH phase. Generally, the composition in pore solution is determined by the dissolution of the clinker phases as well as the sulfate carriers in the cement and the precipitation of the hydration products, such as ettringite, portlandite and
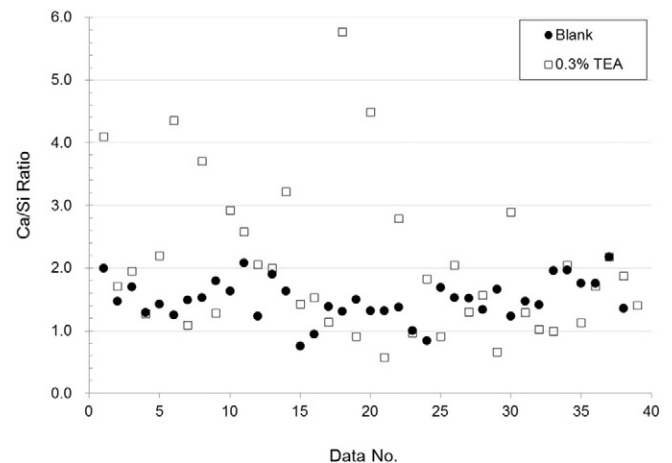

Fig. 9. Calcium-to-silica ratio of the C–S–H phase measured by EDX in hydrating cement pastes without and with addition of TEA at the time points of A1 and B1 respectively.
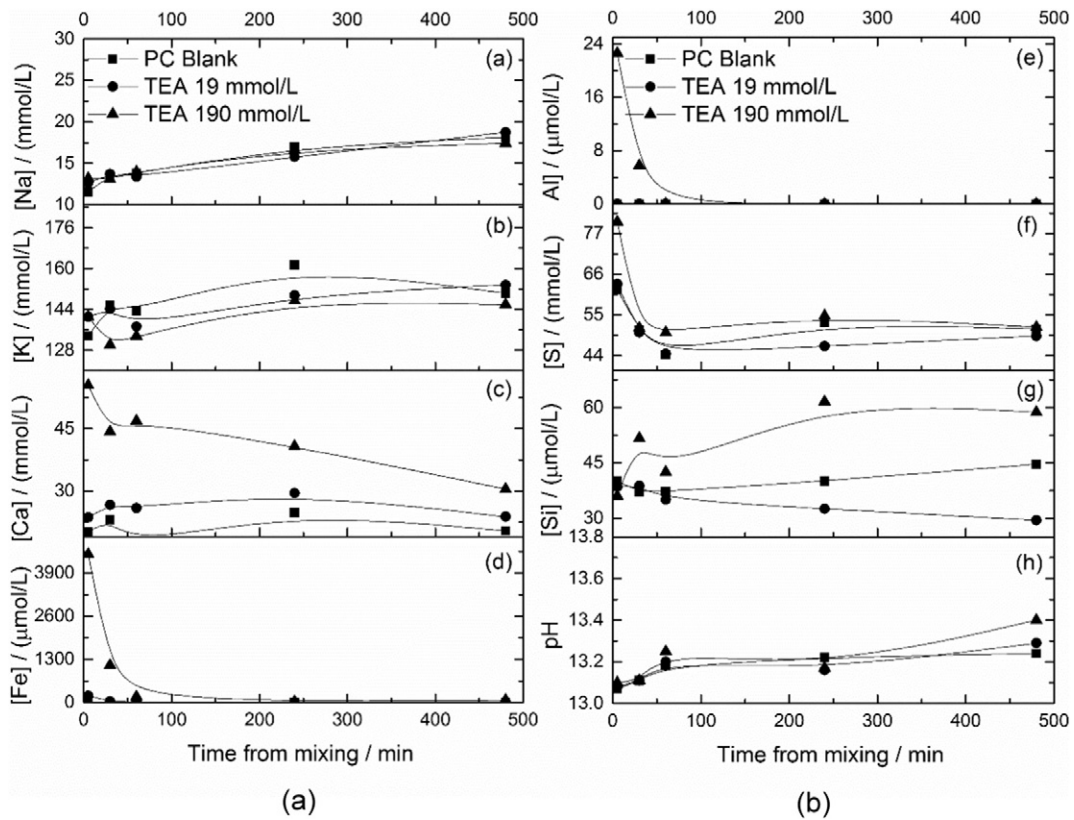
Fig. 10. Effects of TEA on the elemental concentrations in the pore solution of hydrating the cement pastes.

C–S–H. A number of studies dealing with the evolution of the elemental concentrations in pore solution in hydrating Portland cement systems have been published in the last 20 years [13–24]. During the first hours of hydration, the pore solution is dominated by high concentration ions including sodium, potassium, calcium, sulfate and hydroxide in an order of tens to hundreds millimole per liter, together with some low concentration elements such as Al, Fe and Si in an order of several tens micromole per liter. It has been realized that the interaction of TEA with various metal ions (Fe^{3+} and Al^{3+}) in the pore solution of a hydrating cement paste is the key in affecting the cement hydration [2]. On the other hand, as one of the major cationic ions in the pore solution of a hydrating cement paste, calcium ion significantly impacts many aspects of cement hydration, such as the kinetics of cement hydration, microstructure of the hydration products, and even many other macroscopic properties. In this context, the elemental concentrations of the pore solution in the hydrating cement pastes in the presence and absence of TEA were analyzed by ICP-OES.

Fig. 10 exhibits the evolution of the concentrations of different elements with the elapsed time at TEA concentration of 0, 19 and 190 mmol/L in the pore solution respectively. It is clearly found that the elemental concentrations of Ca, Fe, Al, S, Si, are evidently affected by the addition of TEA at concentration of 190 mmol/L, while the concentrations of K and Na are hardly influenced by the presence of TEA. In addition, pH value of the pore solution is almost unaffected in the early hydration period (<4 h) as seen from Fig. 10(h).

Due to the fast dissolution of alkali-sulfate phases, the concentrations of Na, K and sulfate reach very high within a few minutes after contact of cement to water, as seen from Fig. 10(a), 10(b) and 10(f). It is reasonable to believe that the addition of TEA does not influence the dissolution of the alkali-sulfate phases and hence does not visibly affect the concentrations of Na and K. The concentrations of Na and K stay rather stable or slightly increase over time mainly due to the consumption of free water, while the sulfate concentration quickly drops due to the early formation of ettringite.
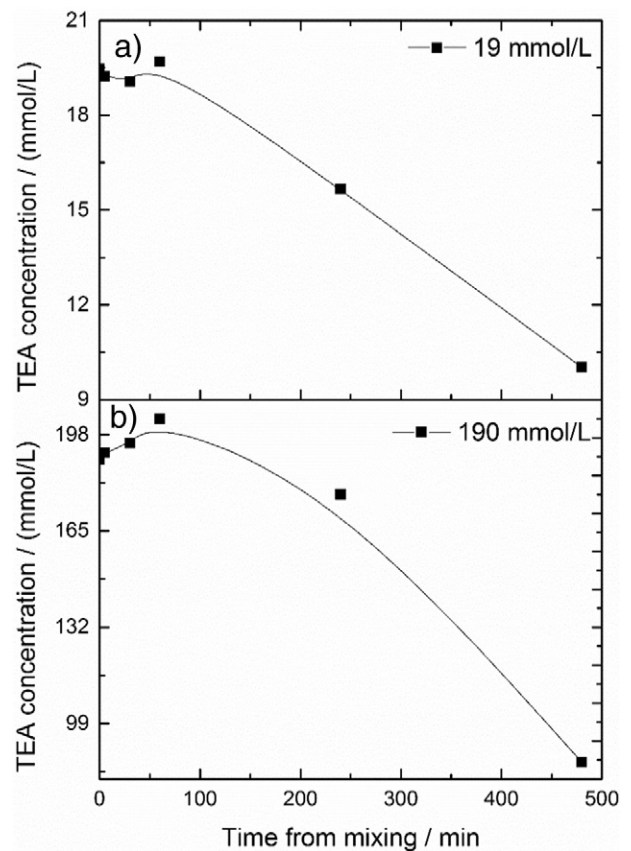

Fig. 11. Evolution of TEA concentration in the pore solution of hydrating the cement pastes: (a) The initial concentration of TEA is 19 mmol/L and (b) the initial concentration of TEA is 190 mmol/L.
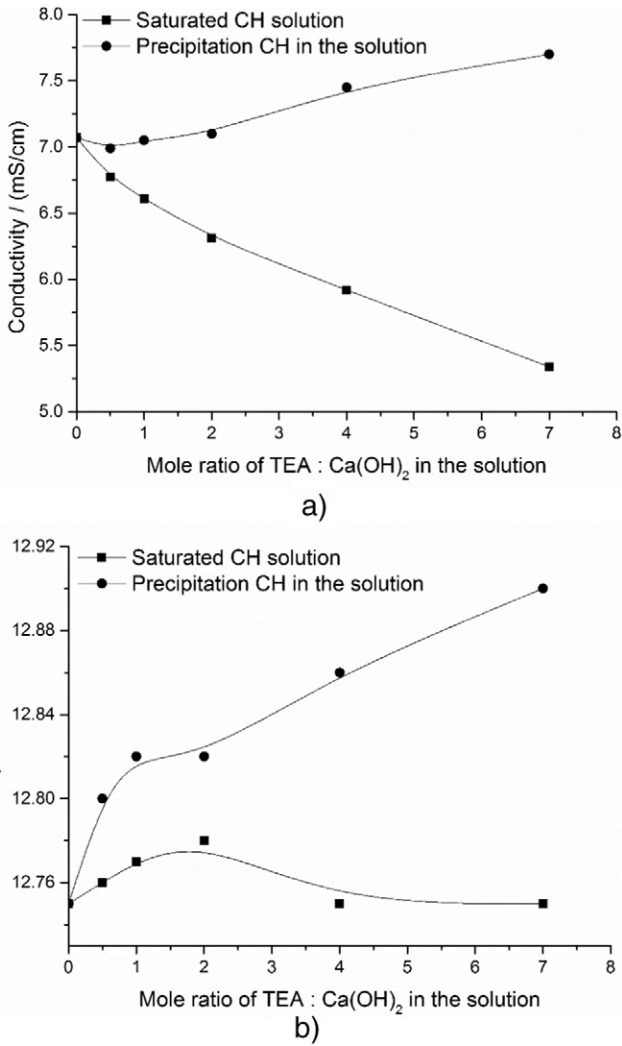
Fig. 12. Influences of TEA on the conductivity (a) and pH value (b) of the saturated Ca(OH)$_2$ solutions with and without the precipitate of Ca(OH)$_2$.
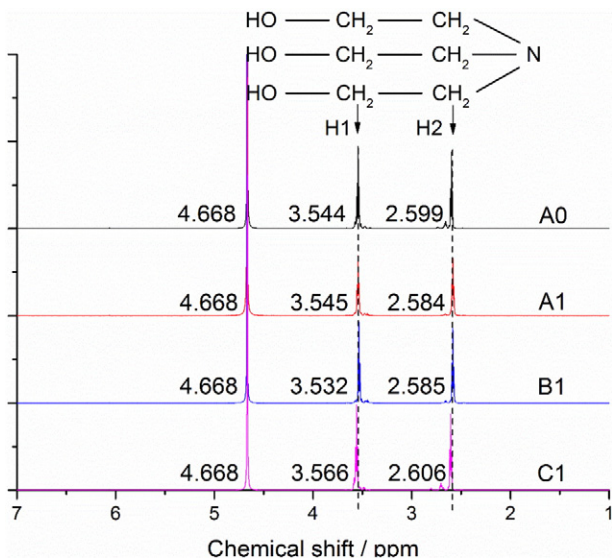

Fig. 14. UV adsorption spectra of TEA solutions with varied Ca^{2+} concentrations.

Fig. 13. ^{1}H-NMR spectra of TEA in D$_2$O solutions in the presence of Ca(OH)$_2$ (A1), KOH (B1) and CaCl$_2$ (C1) respectively.

The concentration of hydroxide is regulated by the alkali ions, namely Na and K to maintain the electroneutrality of the solution. Therefore, the pH value keeps almost constant after it reaches about 13.2 in this study and then slightly increases due to the consumption of free water by the continuous hydration or by the slow release of alkalis that are trapped in the slowly hydrating clinker phases [16]. As discussed above, the dissolution of the alkalis is hardly influenced by the addition of TEA. As a consequence, the pH value should not be affected by the addition of TEA, which is exactly observed in our study as indicated in Fig. 10(h). It is seen that the pH value before 4 h is hardly affected by the addition of TEA. The larger difference of pH values at 8 h (seen in Fig. 10(h)) can be ascribed to the different hydration degree and hence different consumption of free water in the three pastes.

With respect to the concentrations of Fe and Al, they generally remain very low (μmol/L) over a long period of hydration in typical Portland cement [16]. However, as observed in Fig. 10(d) and 10(e), the initial concentrations of Fe and Al are greatly heightened by the addition of TEA, which is consistent with the literatures [2,6]. It has been concluded that TEA accelerates the dissolution and thus the early hydration of aluminate phases, C$_3$A and C$_4$AF, because of the chelating effect of TEA with Al^{3+} and Fe^{3+}.

Regarding the elements of Ca and sulfate in typical Portland cement system, their concentrations usually stay rather stable within several hours (before depletion of sulfate carriers) as they are manipulated by the presence of CaSO$_4$ and Ca(OH)$_2$. This is also observed in Fig. 10 (c) and 10(f). The higher initial sulfate concentration is related to the fast dissolution of sulfate carrier and then it quickly drops to a relatively stable value due to the consumption of gypsum and the precipitation of ettringite. On the other hand, it has been also reported that Ca concentration inversely affects the concentrations of S and Si [17,23]. That is to say, lower Ca concentration corresponds to higher concentrations of S and Si. For example, for high alkali containing cement, higher pH usually gives rise to a lower Ca concentration and consequently leads to higher sulfate and Si concentrations [15,16].

In this study, it is seen from Fig. 10(c) that the Ca concentration in the high TEA containing cement paste is notably increased by the presence of TEA right after mixing and then maintains at higher level compared to the blank cement paste. The elevated initial Ca concentration could be ascribed to the accelerated dissolution of C$_3$A and C$_4$AF, and has been concluded by Gartner and Myers [6] and Perez [2] et al. However, the higher Ca concentration in the presence of TEA at later stage (30 min–8 h) seems somehow incomprehensible since the pH value remains less affected by the addition of TEA during this time period. It is seen from Fig. 10(f) that the initial sulfate concentration is relatively
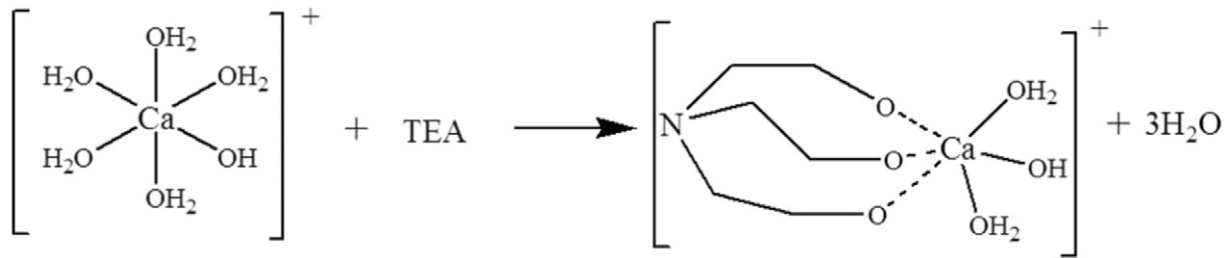
Fig. 15. Schematic drawing on the structure of the chelate complex of TEA with calcium ion.

high due to the fast dissolution of sulfate carriers (gypsum and anhydrite) and then quickly drops, which is because of the subsequent formation of ettringite. In the case of high concentration of TEA being present in the cement paste, the initial sulfate concentration is slightly higher than in the blank system, which is not in line with the higher initial Ca concentration, since the Ca and sulfate concentrations are controlled by the solubility of CaSO$_4$.

In a blank Portland cement system, the Si concentration is usually very low over a long period of hydration and is controlled by the Ca concentration because of the solubility of C–S–H phase. It is seen from Fig. 10(g) that Si concentration in the high TEA containing cement paste is visibly higher than in the blank system over a long period of hydration time, although the initial Si concentrations in the two cement pastes are rather identical. The very low starting concentration of Si is because of the very slow dissolution of the silicate phases in cement.

One of the significant new findings in this study is the elevated Ca concentration by TEA, to which little attention has been paid in the past. In the meantime, concentrations of S, Si are also affected, namely increased by TEA. As discussed above, it is easily understood that the concentrations of sulfate and silicate anions in the pore solution are counter balanced by the concentration of calcium cations through the dissolution-precipitation equilibrium of their corresponding precipitates with Ca^{2+} such as ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O) and C–S–H [14]. That is to say, an increase in the concentration of Ca^{2+} in pore solution is usually accompanied by a decrease in the concentrations of sulfate and Si [17,23]. However, in this study, it is surprisingly found that the concentrations of Ca (from beginning to 8 h), S (at beginning) and Si (from 30 min to 8 h) in the pore solution are elevated by the addition of TEA.

To explain this abnormal phenomenon, it is proposed that the elevated Ca concentration in the pore solution is possibly due to the complexation effect between TEA and Ca^{2+} and such complexation may further shift the precipitation equilibrium of Ca^{2+} with hydroxide, sulfate and silicate anions. We suppose that there might be two types of calcium ions existing in the interstitial pore solution when TEA is present. One is the typical free calcium ion (FCI) and the other one is the chelated calcium ion by TEA molecule, which is called 'chelated calcium ion (CCI)'. Clearly, FCIs have higher precipitability with the hydroxide, sulfate and silicate anions than CCIs. In other words, the integration of TEA in the structure of CCIs increases the solubility of Ca^{2+} ions in the pore solution. Therefore, in the presence of TEA in pore solution, the increased initial sulfate concentration and the Si concentration could be a result of the decreased FCI concentration, although the overall elemental concentration of Ca is elevated due to the formation of CCIs.

As shown in Fig. 11, along with the progressing cement hydration, the TEA concentration in the pore solution remains nearly unchanged in the first hour and then rapidly drops when the cement hydration steps into the acceleration period, which is in good agreement with the literatures [2,6]. It is known that a large amount of CH and C–S–H are produced in the acceleration period, so it is most likely that TEA molecules are adsorbed or incorporated by these hydration products due to the formation of the TEA-Ca^{2+} complexes, which results in the noticeable change of the CH morphology and of the Ca/Si ratio in C–S–H phase.

3.4. Investigation of complexation between TEA and calcium ions by solution experiments

3.4.1. Conductivity and pH value analysis

In order to confirm the complexation between TEA and calcium ions, further experimental investigations on the saturated Ca(OH)$_2$ aqueous solutions with or without TEA were carried out by measurements of conductivity and pH value, as summarized in Fig. 12.

In a neat saturated Ca(OH)$_2$ solution, the addition of TEA leads to a noticeable decrease of the conductivity while the pH value of the solution stays little changed. It is well known that the conductivity of solution is mainly dependent on the ionic concentration and the mobility of the related ions in the solution. If the TEA-Ca^{2+} complex is formed, the mobility of CCIs must be lower than that of FCIs. This way, it is believed that the decreased conductivity is caused by the formation of chelate complex of TEA-Ca^{2+}, which transforms the FCIs into CCIs. Meanwhile, the OH$^-$ group in the solution is unaffected by the complexation process and hence the pH value of solution remains rather stable.

In comparison, the other experiment using saturated Ca(OH)$_2$ solution containing additional undissolved Ca(OH)$_2$ powdering precipitate, shows much different results upon TEA addition as seen in Fig. 12. The addition of TEA results in a notable increase of pH value and hardly affects the conductivity of the solution. This is again in line with the formation of the TEA-Ca^{2+} complex as proposed above. The formation of TEA-Ca^{2+} complex may facilitate further dissolution of the solid Ca (OH)$_2$ and as a result the OH$^-$ concentration is increased by the addition of TEA. The further dissolution of the solid Ca(OH)$_2$ somehow compensates the reduction of the conductivity caused by the formation of CCIs and thus the conductivity of the solution stays little affected. These abovementioned results again provide concrete and convincing evidence of the formation of TEA-Ca^{2+} complex.

3.4.2. ^{1}H-NMR and UV absorption spectra

To further clarify the molecular structure of the chelate complex of triethanolamine and calcium (TEA-Ca^{2+}), ^{1}H-NMR spectroscopy and UV absorption spectra technique were employed to investigate the interaction between TEA and Ca^{2+}.

The ^{1}H-NMR spectra of TEA in D$_2$O solution (A0) is shown in Fig. 13 and two characteristic chemical shifts δ_1 and δ_2 are observed, which respectively corresponds to the hydrogen atoms H$_1$ and H$_2$ in TEA molecules. The addition of Ca(OH)$_2$, KOH, and CaCl$_2$ in the TEA solution causes an obvious alteration in the chemical shifts due to the changes of the chemical environment of the hydrogen atoms, as shown in Fig. 13. The results of ^{1}H-NMR are summarized in Table 3. In comparison with sample A0, one may find that the δ_1 of TEA solution with Ca(OH)$_2$ (A1) remains nearly unchanged whereas the δ_2 of A1 is getting smaller. Correspondingly, the difference between δ_1 and δ_2 in A1 becomes larger. The variations on δ_1 and δ_2 as well as the difference between the two values are certainly caused by the existing of Ca^{2+} and OH$^-$ in the solution. To confirm this, the NMR spectra of TEA in D$_2$O solution containing KOH (B1) and CaCl$_2$ (C1) are analyzed to respectively identify the effects of OH$^-$ and Ca^{2+} on chemical shifts.
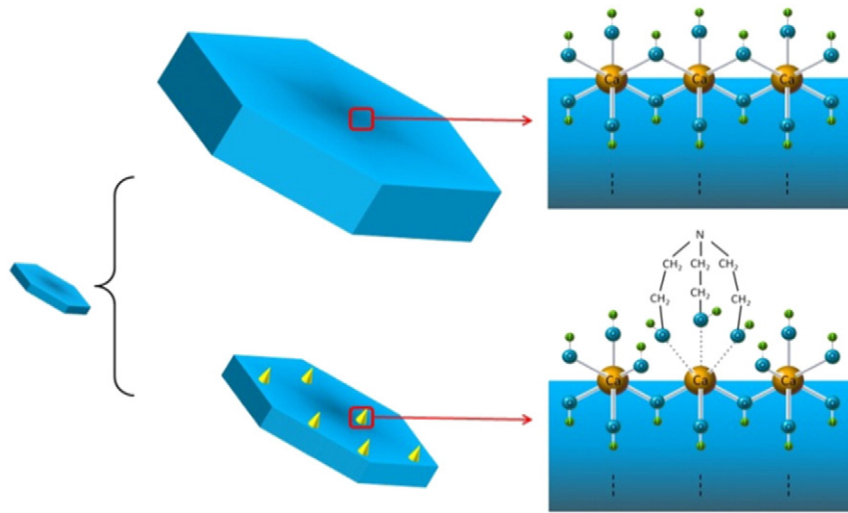
Fig. 16. Schematic drawing of the influence of TEA on morphology of CH.

For the TEA solution with KOH (B1), which has the same pH value as A1, both δ_1 and δ_2 move to lower chemical shifts while the difference between δ_1 and δ_2 keeps nearly constant. Clearly, the lower δ_1 and δ_2 values originate from the electron-donative feature of OH$^-$ in the chemical atmosphere of higher pH [25]. And the constant $\Delta\delta$ implies that there is no specific interaction between the OH$^-$ group (or K$^+$) and the groups in TEA molecules. According to the result of B1, looking back on the results of A0 and A1, we may conclude that the presence of OH$^-$ group (A1) should have caused the decrease of the chemical shifts for both H$_1$ and H$_2$. Thus, the decrease of δ_2 from 2.599 ppm in A0 to 2.584 ppm in A1 can be ascribed to the higher pH value, which is similar to the shift of δ_2 in the tests of A0 and B1. However, the unchanged δ_1 in A1 does not fit to this scheme and suggests that there must be other interaction between Ca^{2+} with the atoms in TEA. From the comparison of A0 and C1, it is noted that the presence of CaCl$_2$ leads to a growth in δ_1 and δ_2 and the increase of δ_1 is much larger than that of δ_2. Knowing that Cl$^-$ has no specific interaction with TEA molecules, we believe that the variation of δ_1 and δ_2 in C1 compared to A0 is solely determined by the selective interaction between Ca^{2+} with the oxygen or nitrogen atoms in TEA. That is to say, there is a calcium–oxygen bond or calcium–nitrogen in the chelate complex of TEA-Ca^{2+}.

With the aim of answering the question whether the complexation of TEA with Ca^{2+} takes place between the Ca^{2+} and the nitrogen atom or the oxygen atom in TEA molecule, the UV absorption spectra of the TEA solutions with varied Ca^{2+} concentration are analyzed as given in Fig. 14. It is clearly seen the main absorption peak of the TEA solution locates at 212 nm, which is caused by the excitation of electrons from n to σ^* of the nitrogen atom in TEA because that of oxygen atoms usually occurs at a wavelength of less than 200 nm. Here, n refers to the lone pair electrons and σ^* denotes the antibonding electrons formed by transition of electron from ground state to excited state. In Fig. 14, with the variation in Ca^{2+} concentration, the main absorption peak almost stays stable, which implies that the nitrogen atom in TEA molecules does not interact with calcium ion in solution. That is to say, the chelating effect between Ca^{2+} and TEA should be ascribed to the specific interaction between the Ca^{2+} ions and the oxygen atom in TEA molecules.

The above provided ^{1}H-NMR and UV results firmly verify the hypothesis of the formation of TEA-Ca^{2+} complex via specific interaction between Ca^{2+} with the oxygen atoms in TEA molecule, as schematically demonstrated in Fig. 15. Similar to the FCIs in the solution, the complexed calcium ions in TEA-Ca^{2+} (CCIs) could also participate in the crystallization process of CH during cement hydration (Fig. 16), which

will distort or even terminate the growth of CH crystals due to the integration of TEA in the phase. As a result, in the presence of TEA, the morphology of CH phase is changed from the lamellar, parallel-arranged crystals with large sizes to distorted crystals with much smaller sizes, and the CH micro-crystals and even the amorphous non-crystalline CH are observed by TEM (Fig. 7).

4. Conclusions

In this paper, a systematic investigation of the influences of TEA on the content and the morphology of portlandite formed during cement hydration was carried out. Based on results of the pore solution analysis and the study on the interaction between TEA and Ca^{2+} ion in solution by NMR and UV, the mechanism of TEA in affecting CH phase was proposed. On the basis of the results above, the following conclusions can be drawn:

(1) The addition of TEA in cement pastes leads to a notable reduction of the measured CH content by XRD and TGA at early ages in a hydrating cement paste.
(2) From the SEM observations, the morphology of CH crystals changes from large and parallel-stacked lamellar shape to smaller and distorted actinomorphic one due to the addition of TEA in the cement pastes. For the first time, the CH micro-crystals and even non-crystalline CH in HCPs in the presence of TEA were observed by TEM and electron diffraction techniques. Remarkable higher Ca/Si ratio of the C–S–H phase in the presence of TEA was found, which was also reported by other researchers and was supposed to originate from the CH micro-crystals embedded in the C–S–H phase during cement hydration.
(3) The pore solution analysis and NMR and UV results evidence the chelating effect between TEA and Ca^{2+} ions via the interaction between Ca^{2+} and the oxygen atoms in TEA molecule. It is supposed that by forming a complex of TEA-Ca^{2+}, TEA can be introduced into the crystallization process of CH phase and thus significantly alters the morphology of CH crystals and even the content of the crystalline CH phase.

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