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Effect of triethanolamine hydrochloride on the performance of cement paste

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HIGHLIGHTS

- Moderate TEA·HCl decreases the water requirement.
- It also shortens the setting times and alters strengths.
- It delays the end time of the induction period.
- Excessive TEA·HCl accelerates AFt conversion to AFm.

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ABSTRACT

Triethanolamine ($C_6H_{15}NO_3$, TEA) is one of the known organic amine accelerators for the cement-based materials. Triethanolamine hydrochloride ($C_6H_{15}NO_3 \cdot HCl$, TEA·HCl), part of whose molecular structure is the same as TEA, can also be regarded as chloride. Thus the water requirement for the normal consistency, setting time, strength, hydration heat liberation, calcium hydroxide (CH) and ettringite (AFt) contents in the hardened paste with TEA·HCl were analyzed and the effect of TEA·HCl on the performance of cement paste was studied to assess the feasibility of TEA·HCl used as an identical accelerator. The results indicate that moderate TEA·HCl decreases the water requirement for the normal consistency and this decline is related to the formation of the absorbed film on the cement particle. Zeta electric potential result also proves the appearance of the absorbed film. It also shortens the setting times and alters strengths. But the alterations of setting times and strengths depend on the TEA·HCl content. Heat liberation result implies that it delays the end time of the induction period and also postpones tricalcium silicate ($3CaO \cdot SiO_2$, C_3S) hydration at early age, however moderate TEA·HCl increases the rate of C_3S hydration in accelerated phase. Excessive TEA·HCl accelerates the AFt conversion to monosulfoaluminate (AFm) after several hours. The conversion product is the AFm with 14 H_2O. TEA·HCl changes the total heat liberation, and these pastes with more TEA·HCl liberate more heat before about 12 h, but this case is reverse after about 12 h. X-ray powder diffraction (XRD) and differential thermal analysis (DTA) results conformably confirm that excessive TEA·HCl delays C_3S hydration and decreases CH content in the hardened paste, but it increases the AFt content in the hardened paste. Hardened pastes with TEA·HCl provide the higher content of AFt than the control even at 28d. Heat liberation, CH and AFt contents are closely responsible for the results of the setting times and strengths. These results will provide a reference for the TEA·HCl application as an accelerator in the practice.

1. Introduction

With more and higher requirements for the construction industry, the need for a concrete with sufficient strength at a very early age in many situations is of great importance [1–3]. In general, there are three main ways to obtain the high early strength. Firstly, special cement, namely high-early-strength cement is one choice but not widely used because of its low yield and high price. Besides, improving the curing can also speed up the binder hydration process to achieve early strength, while there used to be many problems such as the high energy consumption in practical production. Compared to these two ways, accelerator will be the best choice, which plays an important role in improving concrete early performance, increasing construction efficiency and saving the cost. Concrete accelerator is defined as an admixture

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that increases the rate of development of early strength in the cement and concrete mixes with or without dramatically affecting the setting times [4]. Various substances are known to act as early strength accelerators for concrete or cement-based materials. These accelerators which are widely used could be divided into three types: chloride, sulfate and organic amine.

Calcium chloride ($CaCl_2$) is known to accelerate both the setting and hardening of Portland cement concrete and tricalcium silicate ($3CaO{\cdot}SiO_2$, C_3S) phase [5–7], which has long been used since 1885, and it is one of the most widely recognized and used accelerators owing to its ready availability, low cost, and predictable performance characteristics over several decades [8–10]. Particularly, it finds application mainly in cold weather, when it allows the early strength gain to approach that of concrete cured under normal curing temperatures and, probably more importantly, reduces the setting times so that finishing operations can proceed without undue delay. It is usually added at a rate of 0.1–0.7% by mass of cement. The use of $CaCl_2$ is known not only to accelerate the formation of calcium silicate hydrate (C–S–H), but to change its morphology with a low density microstructure [11–13]. However, $CaCl_2$ effectiveness is varied with cement type, and it does not have the same effect on cements with different mineral components [14,15]. Besides, considering the possibility of corrosion, the use of $CaCl_2$ in reinforced concrete containing embedded metal has been critically controversial [16,17], specifically where the concrete is of a porous structure. Many countries have made provision in the relevant codes of practice to prevent or limit its use where steel reinforcement is present. (ACI 318 specifies a maximum chloride limit in concrete of 0.06% by weight of cement to reduce the risk of corrosion (2008) [18], Chinese national code strictly regulates the chloride content in cement should be less than 0.06%). Hence, it has renewed interest and attempt in ‘chloride-free’ accelerators as an alternative to calcium chloride in reinforced concrete.

Sulfate accelerators mainly include sodium sulfate and aluminum potassium sulfate. Sulfate is strong electrolyte, which increases the ionic strength of cement paste and promotes the formation of the hydrated calcium sulphoaluminate. However, more sulfates have to be needed to induce a sufficient increase in compressive strength. Besides, the soluble ions such as K^+ and Na^+ result in remnant in concrete, which will salt out from the surface and further generate expansion and cracking by Alkali-Aggregate Reaction [19]. At the same time, concrete may well be subjected to the sulfate attack. Redundant sulfate ions will react with portlandite, and the reaction product, calcium sulfate further react with hydrated calcium aluminate, both of which will lead to concrete expansion and then cracking.

With respect to organic amine accelerators, most of which are alkanolamines that have been used as additives in cement production and concrete technology for decades. For instance, extensive studies have been carried on the effect of triethanolamine ($C_6H_{15}NO_3$, TEA) on the hydration of Portland cement and its minerals. It was reported that TEA accelerates the hydrations of tricalcium silicate ($3CaO{\cdot}Al_2O_3$, C_3A) and calcium aluminoferrite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, C_4AF), and facilitates the formation of ettringite (AFt) in the C_3A-gypsum-H_2O system during the induction period [20–23], while it retarded the hydration of C_3S [24]. However, it is well known that the behavior of TEA in cementitious system is highly dependent on the content [25,26]. Depending on the cement type and mixing rate, TEA will generate either setting acceleration or retardation. When at small dosage, it acts as setting accelerator; while at higher dosage, it acts as setting retarder; at much higher dosage, it is a strong accelerator. The accelerating-retarding effect of triethanolamine on the initial setting time is caused by the different intensity of formed AFt, which is governed by the triethanolamine dosage [27]. Xu et al also reported that TEA increases the rate of the second hydration of C_3A [28–32] and this case is similar to that reported by the Yaphary et al. [27]. Even in the other systems such as steel slag-blended cementitious materials and sodium silicate/hydrated cement, it can also accelerate the hydrations of these systems [33–36]. Meanwhile these reports addressed that hydration accelerations of these systems are closely related to the AFt formation. At present, TEA is usually used with other inorganic accelerators as an ingredient in some admixture formulations [4,37], and it turns out to be a good choice. Triethanolamine hydrochloride ($C_6H_{15}NO_3{\cdot}HCl$, TEA·HCl) is a white crystal with layered structure, part of whose molecular structure is the same as TEA, TEA·HCl also can be regarded as chloride. But little chlorine contains in it as compared with the $CaCl_2$. In theory, it can be used as a compound accelerator with two kinds of acceleration effect simultaneously. However, little study and literature paid attention to its influence on the hydration of cementitious system. Besides, although there are many reports related to TEA, the accelerating setting/hydration mainly attributed to the AFt formation in these reports. There may have some other cases which lead to the quick setting, however these cases are not found from these reports. Moreover, the cost of TEA preparation is relatively higher than other hardening accelerators. However, the cost of TEA·HCl is less than that of TEA. Thus extensive tests such as water requirement for the normal consistency, Zeta electric potential, setting time, strength, hydration heat liberation, calcium hydroxide (CH) and AFt contents in the hardened paste were tested in this work to access the feasibility of TEA·HCl used as an identical accelerator, meanwhile the mechanism of the accelerating setting/hydration is also addressed in this work.

2. Materials and experimental procedure

2.1. Materials

In this study, cement was provided from Helwan Portland Cement whose chemical compositions and particle size distribution (Median diameter: 18. 5 μm, Mean diameter: 22.8 μm) are respectively given in Tables 1 and 2. TEA·HCl is a chemical reagent and it was provided by the China National Pharmaceutical Industry Corporation Ltd. The effective content of TEA·HCl is about 99.99%.

2.2. Sample preparation

In all tests, paste was prepared according to the water requirement of normal consistency. Besides, mortar was prepared with same water/cement (0.5) and sand/binder (3.0). Different contents TEA·HCl were employed in paste and mortar, contents and their corresponding number are listed in Table 3. Deionized water was used in all experiments in this study including the preparation of cement pastes.

2.3. Methods

2.3.1. Physical and mechanical performance tests

The water requirement of normal consistency and setting time of cement pastes with and without TEA·HCl were measured by a Vicat apparatus according to the Chinese national standard GB/T1346-2011. And the results of water requirement of normal consistency test were proportionally applied to subsequent paste experiments. Mechanical strength tests of mortars with and without TEA·HCl were carried out at the age of 3, 7 and 28 days in accordance with the Chinese national standard GB/T 17671-1999. Mortars were prepared by using a 40 mm × 40 mm × 160 mm prism specimen with a sand/binder ratio of 3.0 and a water/binder ratio of 0.5. And then, these molded specimens were cured on standard condition ($T = 20 \pm 2$ °C, RH $\geq$ 90%) for certain ages before strength test.

2.3.2. Zata electric potential

Zeta electric potential of cement solution with TEA·HCl was conducted at 25 °C using a ZETASIZER Nano series instrument (Malvern Instruments). First, the raw material was weighed according to the experimental proportioning. Cement was put into the mixer, and then the water was added to the mixer for 2 min at low speed. Next, the corresponding output TEA·HCl was added, and the cement grout was made in the high speed stirring for 2 min. And a small amount of cement grout was diluted 3000 times with water and stirred to form a clarification solution. Finally, the 3–5 ml clarification solution was picked to be tested.

Table 1
Chemical compositions of reference cement (wt, %).

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	SrO
Content	0.08	2.65	4.58	19.9	0.11	2.42	0.06	0.86	61.9	0.23	0.05	3.12	0.05

Table 2
Particle size distribution of reference cement (μm).

Volume distribution (%)	<10%	<25%	<50%	<75%	<90%
Particle size	4.2	8.2	18.5	33.2	49.7

Table 3
Label of paste/mortar with different content TEA·HCl.

Content/%	0	0.01	0.015	0.02	0.06	0.10	0.20	0.50	1.00
Number	H0	H1	H2	H3	H4	H5	H6	H7	H8

2.3.3. Isothermal calorimetry

In order to determine the effects of TEA·HCl on cement hydration, an eight-channel isothermal calorimeter (TAM air C08) was used to quantify the cement hydration. The device is based on the differential measurement of the thermal power and produced heat which are proportional to the rate and extent of reaction respectively [38]. The cement paste was prepared directly in the calorimeter sample cup by using 100.00 g reference cement and 50.0 g water with or without TEA·HCl conditioned in the calorimeter (at 20 °C) for at least 2 h prior in order to ensure a precise cement content and a temperature close to the measurement temperature. All tests were performed for measuring hydration heat up to 3d.

2.3.4. AFm identification

The mineralogical phases of hardened pastes were characterized by using X-ray diffraction (XRD). FT scanning was performed on the samples at a 2θ range of 5–70°. Before XRD analysis, the 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.

2.3.5. CH content

The CH contents of mixtures at different hydration ages were measured by differential thermal analysis (DTA). Netzsch STA 409 Thermal analyzer was used with an atmosphere of oxygen-free nitrogen and at a heating rate of 10°/min. Comparing the DTA curves area of the hardened pastes with which of the pure CH, CH contents in the hardened samples were determined by the following Eq. (1)

$$CH = \frac{S_{\mathrm{CH\ in\ mixture}}}{S_{\mathrm{pure\ CH}}} \times 100 \tag{1}$$

where CH is the CH content in the mixtures; $S_{\mathrm{CH\ in\ mixture}}$ is the DTA curves area of the hardened pastes; $S_{\mathrm{pure\ CH}}$ is the DTA curves area of pure CH.

2.3.6. AFt content

The laboratory X-ray powder diffraction patterns (LXRD) were recorded in Bragg-Brentano reflection geometry (θ/2θ) on a Rigaku X-ray diffractometer (D/-max2550VB3+/PC from Rigaku International Corporation, Japan). All the above patterns were refined by the Rietveld method with GSAS-EXPGUI or TOPAS software. Internal standard method was used in this work and finally, the AFt content was Rietveld quantified.

3. Results and discussions

3.1. Water requirement for normal consistency

Water requirements for normal consistency of pastes with TEA·HCl are given in Fig. 1a. It can be observed from Fig. 1a that it has a remarkable effect on the water requirement for normal consistency. Less than 0.1% TEA·HCl decreases the water requirement. But more than 0.1% TEA·HCl increases it. Normally, cement water requirement mainly involves the filled water between cement particles, the adsorbed water on the cement particles and chemical bonded water for the cement mineral hydration. The filled water depends on the cement particle shape and gradation. Absorbed water lies on the cement specific surface area. In this study, the same cement was used and then the water requirement for normal consistency incurred by the cement characteristic can be ignored. But these organic admixtures such as the water reducer or accelerator, they can absorb on the cement particles and then an absorbed film is formed on the cement particle [39]. Zeta electric potentials of pastes with TEA·HCl are shown in Fig. 1b. It can be found from Fig. 1b that it changes the zeta electric potential of cement paste, and paste with more TEA·HCl provides a higher zeta electric potential absolute value. This result implies that it is absorbed on the cement particle and an absorbed film is formed as it is mixed. Moreover, the paste appears a higher zeta electric potential and this film become thicker while there are more TEA·HCl in the mix. The cement particles repel each other for the strong charger. As a result, the paste with it shows a good fluidity and then less water to keep the same consistency. However, it also accelerates the cement hydration. Moreover, the hydration acceleration is more remarkable as more TEA is available in the paste. Thus the chemical bond water in the test process is increased, and then the water requirement increase as more TEA is mixed in the paste. Thus it is different from the pastes with 0.01%, 0.015%, 0.02%, 0.06% and 0.1% TEA·HCl that these pastes with 0.2%, 0.5% and 1% TEA·HCl provide with a higher water requirement than control.

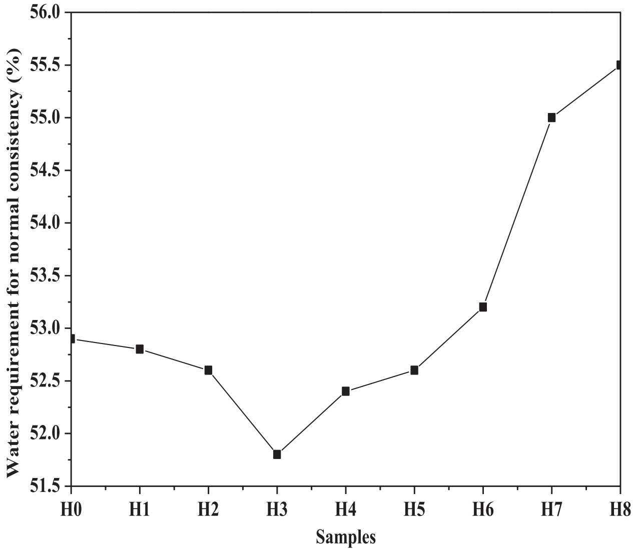

Fig. 1a. Water requirements of pastes with TEA·HCl.

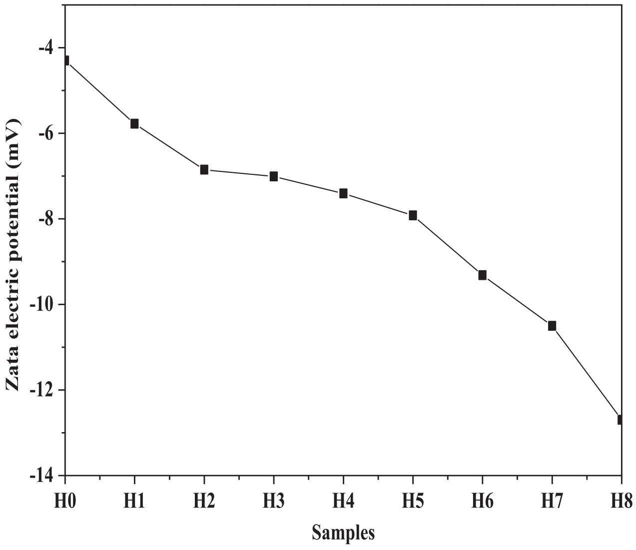

Fig. 1b. Zeta electric potential of pastes with TEA·HCl.

3.2. Setting time

Setting times are main parameter governing the operation schedule for transporting, placing, consolidating and finishing processes of concrete [40–42]. Therefore, the setting times of pastes with TEA·HCl were performed in this work and the results are shown in Table 4. The results indicate that it poses an important impact on the cement setting times and this effect is closely dependent on its content. It acts as a setting accelerator at small dosage (e.g. <0.02%, mass percentage); it postpones the setting time compared to the paste with 0.02% at a higher dosage (e.g. 0.06%); it is a strong accelerator at much higher dosage (e.g. >0.06%), setting times shows a continuously downward trend with the increment of TEA·HCl dosage, especially when dosage is 0.5% and 1%, the initial setting time is less than 20 min. These cases are similar to that of TEA. On the basis of previous researches about the effect of TEA on the setting time and cement hydration, it could be deduced that when dosage is less than 0.02%, TEA·HCl accelerates C_3A hydration and C_3A-gypsum reaction by promoting formation of aluminate hydrate and AFt; 0.06% TEA·HCl results in aluminate hydrate building up and covering on the surface of cement particles, setting time is extended slightly. Besides, strong accelerating effect of much higher dosage on setting time is ascribed to AFt or other new phase formation during accelerated C_3A hydration. Much water is consumed in this hydration and then the paste is lead to a flash set.

3.3. Strength

The compressive and flexural strengths of cement mortars with different contents of TEA·HCl were determined and the results are shown in Fig. 2a and b respectively. The results prove that it alters the strength of hardened paste. Compressive strengths of control at 3d, 7d and 28d are 28.22 MPa, 30.23 MPa and 48.14 MPa respectively. Among all specimens, the hardened paste with 0.02% TEA·HCl provides a highest compressive strengths of 34.62, 41.39 and 51.35 MPa at 3d, 7d and 28d respectively. These values are significantly higher than that of the control and increase by 22.68%, 36.92% and 6.67% respectively. Less than 0.02% TEA·HCl increase the compressive strength. More than 0.02% TEA·HCl plays a negative role on the compressive strength, but pastes with 0.06%, 0.1% and 0.2% still provide a higher compressive strength at 3d and 7d than the control. As shown in Fig. 2b, flexural strength appears a keeping increase as TEA·HCl dosage is less than 0.02%, and the reverse case is observed while the content is more than 0.02%. Flexural strength shows the most significant increase while the dosage is 0.02%. The flexural strengths of sample with 0.02% TEA·HCl at 3d, 7d and 28d are 7.59, 7.74 and 8.05 MPa respectively. But flexural strengths of control at 3d, 7d and 28d are 5.88, 6.47 and 7.26 MPa respectively. Then, the flexural strengths of sample H3 at ages of 3d, 7d and 28d are increased by 29.08%, 19.63% and 10.88% respectively, as compared to control. Flexural strength shows a similar variation to the compressive strength as the content of TEA·HCl is various. It can be found that the strength

Table 4
Setting times of pastes with TEA·HCl.

Setting times (min)	H0	H1	H2	H3	H4	H5	H6	H7	H8
Initial setting time	141	125	120	124	115	59	31	10	7
Final setting time	218	208	201	210	202	182	133	32	24

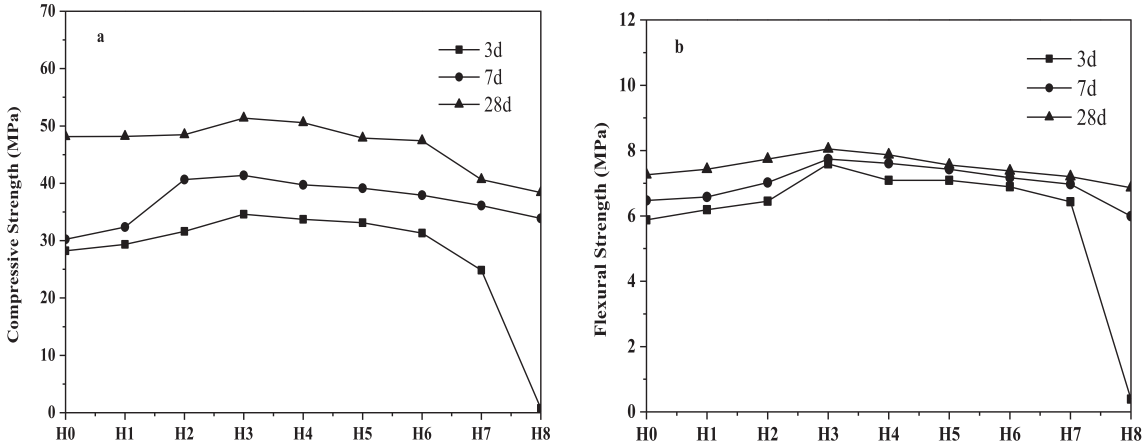

Fig. 2. Compressive and flexural strengths of cement mortars with different contents of TEA·HCl.

increment at the 3d is the most, and the followings are these at 7 and 28 respectively as comparing all strength increase ratios. This result indicates that TEA·HCl has a positive effect on the early strength while the content is low. Overall, 0.02% is a best mixing amount to improve the strength.

3.4. Hydration heat

Cement hydration is a thermodynamic reaction, and it is accompanied by the generation of hydration heat. The hydration heat liberation was also measured during 3d as shown in Fig. 3. Heat liberation is rather intense within a few minutes mainly for the initial rapid hydration of C_3A and C_3S in the pre-induction period (Fig. 3a). Soon thereafter, the overall rate of hydration is slowed down and almost zero in the induction period and then a second main exothermic peak appears as a main result of further hydration for C_3S (Fig. 3b), a third exothermic peak mainly comes from the further reaction for the C_3A, corresponding to the conversion of AFt to AFm (Fig. 3b). The end time of the induction period has an important effect on cement hydration properties. It is found from Fig. 3c that TEA·HCl obviously delays the end time of the induction period. These pastes with TEA·HCl later enter into the acceleration period than the control. Especially, this case is more certain for the pastes with 0.1% and 0.2% TEA·HCl. Normally, the end time of the induction period is mainly responsible for the beginning of C_3S further hydration. Thus the later end time of the induction period provides a proof for the prolongation of C_3S further hydration in these pastes with TEA·HCl. However, the different case can be also observed that these pastes with 0.5% and 1% TEA·HCl have a short end time of induction period. The induction periods of the pastes with 0.5% and 1% TEA·HCl are over at about 3 h and 5 h respectively.

Cement hydration enters into acceleration period after the induction phase. The control provides a distinct second main exothermic peak at about 12 h as shown in Fig. 3b. The peaks of pastes with 0.01%, 0.015% and 0.02% TEA·HCl can be also found at about 12 h. However, the peak of paste with 0.06% TEA·HCl becomes indistinct, and the peaks of pastes with 0.1% and 0.2% TEA·HCl disappear and this peak merges with the third exothermic peak. The particular case is found for the pastes with 0.5% and 1% TEA·HCl and the second main peak does not appear at the 10–20 h as shown in Fig. 3a. The second peaks of pastes with 0.5% and 1% TEA·HCl appear at 5–8 h and 3–6 h respectively. The paste with 0.5% TEA·HCl provides a peak after about 40 h, and this peak may be main exothermic peak of C_3S hydration. This peak change may come from two points. The one is related to the acceleration conversion of AFt to AFm and another point is attributed to the prolongation for the C_3S hydration at early ages while more contents of TEA·HCl are mixed. In order to further explore the mechanism, the paste with 1% TEA·HCl cured for 4.5 h was identified by XRD, and the result is shown in Fig. 4. The characteristic peaks appeared at 9.091, 15.784 and 22.943 2θ are found as the AFt. Besides, the characteristic peaks of AFm with 14 H_2O are found at the 9.25, 31.081 and 32.501 2θ [43]. This result indicates excessive TEA·HCl leads to the conversion of AFt to AFm early. But this AFm is composed of 14 H_2O and it is the common one with 12 H_2O. Normally, AFm formation at the paste plastic stage easily leads to a flash set. So the pastes with 0.5% and 1% TEA·HCl provides a short setting time.

Besides, these pastes, which have the visible second main exothermic peaks at about 12 h, present a different rate of heat liberation. Obviously, the control provides a low rate of heat liberation at this time. The followings are pastes with 0.02%, 0.01%, 0.015%, 0.06%, 0.1% and 0.2% TEA·HCl respectively. This result

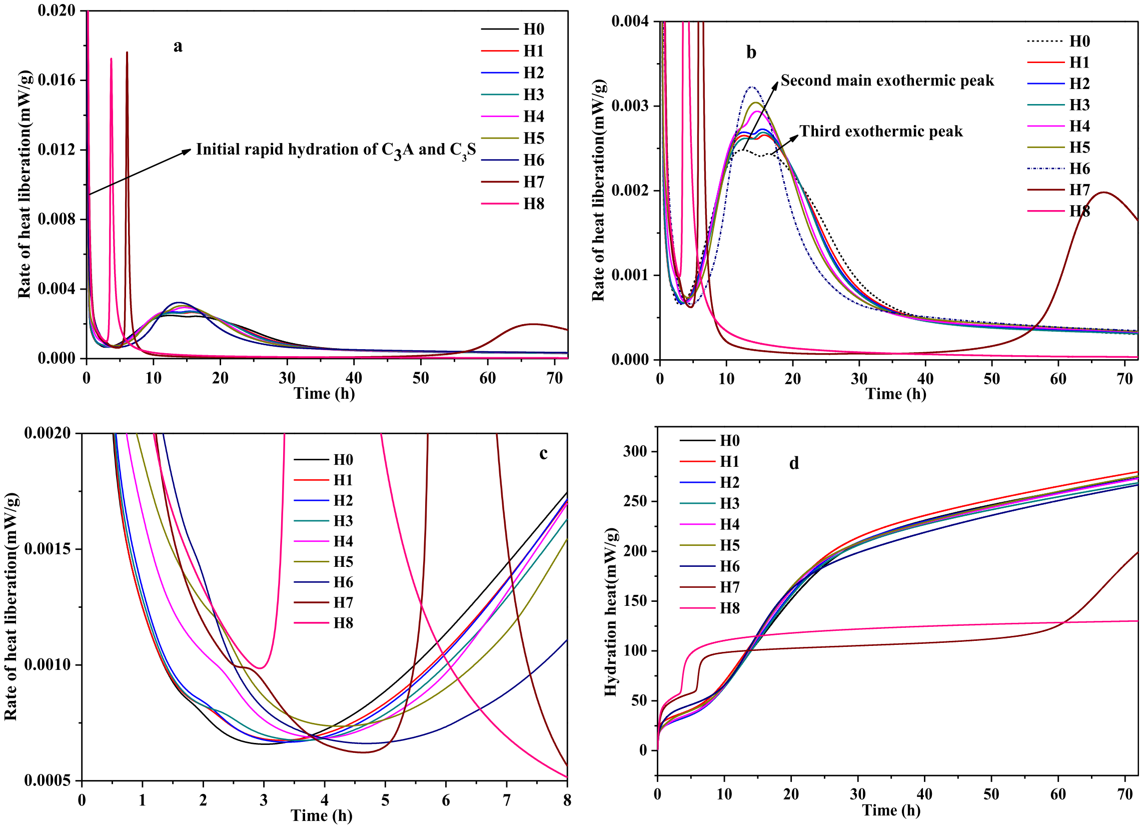

Fig. 3. Heat of hydration curves for cement mortar.

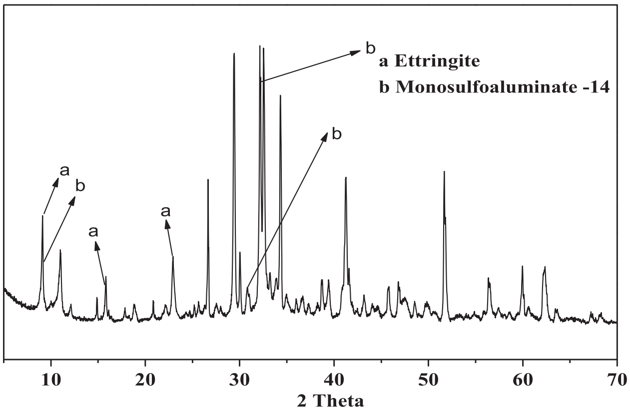

Fig. 4. XRD characteristic peak of pastes 1% TEA·HCl after 5 h.

manifests that TEA·HCl improve the C_3S hydration at this time. However, the pastes with 0.5% and 1% TEA·HCl do not appear something at this time.

The hydration heats of pastes with different contents of TEA·HCl are given in Fig. 3d. It can be observed from this Fig. 3d that TEA·HCl has an important influence on the total cement hydration heat liberation in the 3d. The pastes with 0.5% and 1% TEA·HCl liberates more heat than others at early age. The heat liberation of paste with 1% TEA·HCl is the most and the following is the paste with 0.5% TEA·HCl before about 12 h. However, these pastes with 0.01%, 0.015%, 0.02%, 0.06%, 0.1% and 0.2% TEA·HCl liberates more heat than them after about 12 h. Liberation heat of paste with 0.5% TEA·HCl gradually increase after 40 h and it exceeds the one of paste with 1% at about 60 h and it is rapidly increased later. These results implies that excessive TEA·HCl delay cement hydration at early ages.

3.5. CH content

As one of the main hydration products, CH content in hardened cement paste is closely related to the degree of cement hydration and a higher CH content corresponds to a larger hydration degree [41,44]. In order to further illuminate the effect of TEA·HCl on the cement hydration, CH contents in different hardened pastes were determined after they were cured for 3 and 28d and the result is given in Table 5. The result indicates that TEA·HCl has an important influence on the CH content in the hardened paste.

Overall, TEA·HCl decreases the CH content in the hardened paste. Especially, these pastes with 0.5% and 1% TEA·HCl provide only 1.34% and 1.11% CH at 3d, 5.54% and 3.83% CH at 7d, and 12.97% and 11.82% CH at 28d respectively. The same case can be also found from Fig. 5 (XRD characteristic peak at about 18° of CH in pastes with different contents of TEA·HCl). The peak position of CH XRD peak is also related to the powder surface flatness. Although the peak position of CH is changed, it does not affect the peak intensity of CH at this 2theta. In the paste with 0.5% and 1% TEA·HCl, there is not any CH found at 3d as shown in Fig. 5 3d. There is some CH found in the paste with 0.5% TEA·HCl, however, the paste with 1% TEA·HCl is kept still as shown in Fig. 5 7d. There are some CH in the pastes with 0.5% and 1% TEA·HCl at 28d as shown in Fig. 5 28d. CH mainly concerns to the hydration of C_3S at early ages. Thus this result implies that TEA·HCl observably delays the C_3S hydration. Besides, the case can be also found from Table 5 that more TEA·HCl pose a more remarkable role on the C_3S hydration. As a result, the second main peak (normally, this peak is responsible for C_3S hydration) of paste with 1% TEA·HCl entirely disappears at the 3d and this peak (namely, the third peak of H7) appears after 40 h for the paste with 0.5% TEA·HCl. This result further proves that the second peaks of pastes with 0.5% and 1% TEA·HCl after 5–8 h and 3–6 h respectively are responsible for the conversion of AFt to AFm and TEA·HCl leads to the AFm production at early ages. These cases provide some proof for the strength alteration of hardened paste with TEA·HCl. The hardened pastes with 0.5% and 1% TEA·HCl provide with lower strength at 3d than the control for the fact that excessive TEA·HCl seriously delay the C_3S hydration at the early ages and then little CH appears in the hardened pastes with 0.5% and 1% TEA·HCl.

3.6. AFt content

AFt contents at different ages in the hardened pastes with different contents of TEA·HCl were tested and the result are given in Table 6. It can be seen from Table 6 that TEA·HCl has a prominent impact on the AFt contents at different ages in the hardened pastes with it. The AFt contents of the pastes with 0.01%, 0.015%, 0.02%, 0.06% and 0.1% TEA·HCl at 3d are higher than that of control. The paste with 0.02% TEA·HCl provides the highest AFt content among all pastes. When less than 0.02% TEA·HCl is mixed, AFt

Table 5
CH contents at different ages in the hardened pastes with TEA·HCl.

CH content (%)	H0	H1	H2	H3	H4	H5	H6	H7	H8
3d	14.18	14.1	13.96	13.8	12.55	10.43	8.63	1.34	1.11
7d	17.17	17.09	17.02	15.98	13.05	12.43	11.98	5.54	3.83
28d	18.14	18.13	18.05	18.01	17.56	16.62	13.98	12.97	11.82

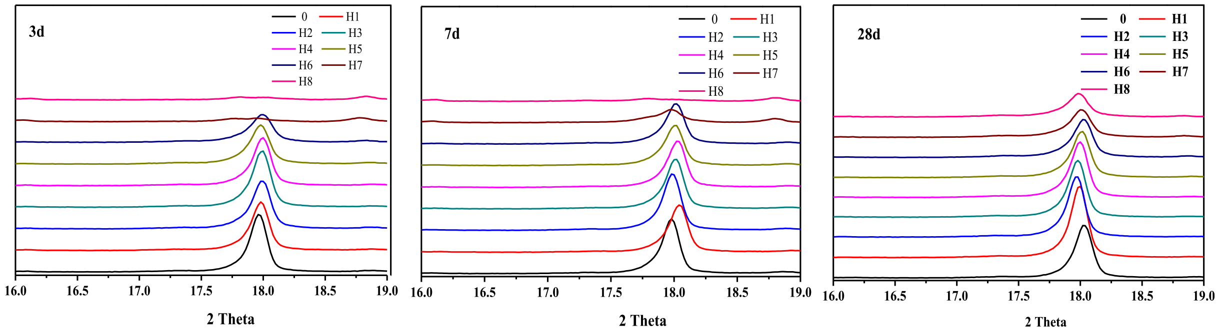

Fig. 5. XRD characteristic peak at about 18° of CH in pastes with different contents of TEA·HCl.

Table 6
AFt contents at different ages in the hardened pastes with TEA·HCl.

Content (%)	H0	H1	H2	H3	H4	H5	H6	H7	H8
3d	7.8	7.9	8.2	8.8	8.5	8.1	7.7	6.8	6.4
7d	6.9	6.8	7.0	7.2	7.3	7.1	6.9	6.1	5.8
28d	3.9	3.9	4.2	4.4	4.5	4.7	4.9	4.9	5.0

content in hardened paste increases as increment of TEA·HCl. However, this case is reversed as more TEA·HCl is introduced. The paste with 1% TEA·HCl provides the lowest AFt content and this value is low that of the control by 1.4%. As already mentioned, TEA·HCl facilitates the conversion of AFt to AFm at the early ages. Thus lower content of AFt at 3d in these pastes with more 0.2% TEA·HCl come from the results of conversion of AFt to AFm. But this fact is sure that overall, it increases the AFt formation at early ages. As a result, the paste with moderate TEA·HCl has the higher strength at early ages such as 3d and 7d than the control. Besides, the case can also be observed from the result related to the AFt contents at 7d that except for these pastes with 0.2%, 0.5% and 1% TEA·HCl, these pastes with more TEA·HCl present a more decline of AFt content from 3d to 7d. The result indicates that it also promotes the conversion of AFt to AFm even at 7d. However, these pastes with less TEA·HCl show a more prominent decrease after 28d and the pastes with more TEA·HCl provides more AFt. This result indicate that overall, TEA·HCl accelerates the AFt formation and increase AFt content. So these pastes with moderate TEA·HCl provide a higher strength than control at 3d and even these pastes with excessive TEA·HCl do not have much lower strength at 7d.

4. Conclusions

This study investigated the effect of TEA·HCl on the hydration of cement. Some conclusions can be drawn as following.

Moderate TEA·HCl benefits the reduction of water requirement for the normal consistency and this reduction is related to the formation of absorbed film on the cement particle. The zeta electric potential result also proves the appearance of absorbed film and the thicker of this film lies on the TEA·HCl content.

It cuts down the setting times and affects the strength. But these cases closely depend on the TEA·HCl content.

It postpones the end time of the induction period and delays the C_3S hydration at the early age, however moderate TEA·HCl increases the C_3S hydration in the accelerated phase. Excessive TEA·HCl accelerates the conversion of AFt to AFm after several hours. The conversion product is the AFm with 14 H_2O. TEA·HCl changes the total heat liberation and cement pastes with more TEA·HCl liberates more heat before about 12 h, but this case is reverse after about12h. Excessive TEA·HCl delays the C_3S hydration

It decreases the CH content in the hardened paste. However, it increases the AFt content in the hardened pastes. The hardened pastes with TEA·HCl provide higher content of AFt than the control even at the 28d. The heat liberation, CH and AFt content are closely responsible for the results of the setting time and strength.

Overall, 0.02% should be the selective dosage in the TEA·HCl practice for the fact that the paste with 0.02% TEA·HCl has the lower water requirement for the normal consistency and higher strength as well as the little reduction for the setting times.

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the word submitted.

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