Effects of Triisopropanolamine and Triethanolamine on Some Properties of Portland Cement

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Abstract

One of the most interesting topics relevant to Portland cement that has attracted many researchers' interest is finding the solution for enhancing the strength of Portland cement, especially strength in early age. Using additives for enhancing early strength of Portland cement is regarded as a good solution. In this study, a mixture of trisopropanolamine (TIPA) and triethanolamine (TEA) was added in cement in the range of 0.020-0.035% to investigate the effect of this mixture on the properties of Portland cement. The results showed that the fineness of cement with the combined additive (TIPA + TEA) was higher than that of an individual one (TEA) and that of ordinary cement. With a suitable amount of additive, the consistency increased, the setting time decreased, the strength of cement enhanced when compared with ordinary cement. Compressive strength of cement prepared with a combined additive (0.01% TIPA + 0.02% TEA) at 1 day of age was the highest (with an increase of 24.21%).

Keywords: Additive, triisopropanolamine, triethanolamine, strength, cement.

1. Introduction

Portland cement has been studied for decades and many researches are still going on to improve its technology and quality [1,2]. Cement strength enhancing has been researched at almost every stage from manufacturing process to using process of Portland cement. Using additives for enhancing early strength of Portland cement is regarded as a good solution [3-10]. There are many additives are used in the manufacture of cement with various targets, in which, there are 3 main types: processing admixture, mineral additives, and mineralization admixture. Processing admixture is added to the grinding process to improve the technology and the properties of cement. The use of processing admixture in cement production has improved the conductivity of grinding machines, reduced clotting powder, created flexible blow, and contributed positively to treating industrial wastes, reducing CO_2 emission and saving energy resources [3-6]. To solve problems about increasing the milling capacity, increasing strength, reducing the clot, and improving the flexibility of cement, we need to add a suitable amount of processing admixture.

The popular processing admixtures used in cement technology are triethanolamine (TEA) and triisopropanolamine (TIPA) [4-6]. Alkanolamines are amines containing a single, double, or triple hydroxyalkyl group, which are frequently used as concrete admixtures and grinding aids additives [7]. TEA and TIPA are known as 2 organic grinding aids. Their nature is surfactants, their molecules are both hydrophobic and hydrophilic. They can absorb the surface of particles, create a film separating particles, reduce the free energy of the surface of the system. On the other hand, they also change the suction force of Van der Waal, increase the thrust, thereby improve the crushing efficiency [3,5-7].

The surfactant molecules penetrate the wedge-shaped micro-cracks on the surface of the material, by means of a force of attraction that they move along the surface of the adsorbent layer. Because of the ability to create a dividing surface, the surfactant molecules are coated with a uniform adsorption layer over the entire surface inside the defects of the material and weaken the intermolecular forces of the particles, making the process of splitting and destroying them easier. Thus, it can be understood simply that because of surface-active additives, the cracks expand, soften the surface layer of solid objects, which is favorable for their destruction when grinding and crushing [3].

TEA was largely used in the preparation of plasticizers for concrete in order to offset the retarding action of other components. TEA is a surfactant, it adsorbs onto the surface of cement particles and the hydration product. TEA can also dissolve some metal ions such as Fe^{3+}, Al^{3+}, so increasing the activity of C_4AF mixture and inhibiting the formation of $Fe(OH)_3$, $Al(OH)_3$ on the cement surface (Fig. 1).

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Thereby promoting the hydration of silicates and aluminates to occur rapidly [3].

TEA can be either a stimulant or an inhibitor of the response, depending on the amount used. Many previous studies have shown that chemical interactions occur as follows:

+ When TEA is present, the reaction between C_3A and gypsum is accelerated. The subsequent conversion of ettringite to hydrogen calcium monosulphate aluminate by reaction with C_3A is also accelerated by TEA.

+ Hexagonal hydrate aluminate formation and transformation to cubic form are also accelerated by TEA.

+ There can be a complex effect by reacting TEA with the ferrite phase in XMP.

There is some evidence for the formation of a complex surface between C_3S, C_2S initial hydrate and TEA. [7].

When TEA is added, it promotes the formation of C-S-H with a higher C/S ratio, increases the formation of non-crystalline $Ca(OH)_2$, and improves the specific surface of the hydration product. TEA has the effect of retarding the initial hydration, but the mechanism of action of TEA on the different components of cement has not been established and it may be due to a layer of protection formed on the surface of the hydrolytic phases, protection for silicates and aluminates, reduction of reaction rates [8].

TEA-based grinding aid improved cement quality, especially 1-day strength, they tested its effect with cement containing gypsum on hydration. This process is evident in the heat of hydration data. Two different cementitious samples were used: one consisting of 5% gypsum, clinker and TEA, the other containing 5% gypsum, clinker and non-TEA. Both mixtures are mixed with water, water/cement ratio is equal to 0.5. Fig. 2 shows the first two peaks. The first is very sharp, which is thought to be the stage of hydrated sulfoaluminate formation, the reaction is completely exothermic. The second is broad and involved in the formation of free lime and CSH, development of the mechanical properties of cement.

The above analysis clearly shows that TEA acts as an accelerator for C_3S hydration, thus enhancing the early strength of the cement. Morphological analysis of the cement paste shows that the sulfoaluminate gel has the same structure in each stage. But comparing the structures at one time of hydration, in the case of clinker with TEA, the hydration of C_3S, and then the growth of CSH was faster, and after 4h the crosslinks were complete by gel structure [9].

Triisopropanolamine (TIPA) is a tertiary amine used in the cement industry as a grinding aid and in formulas of concrete. The action mechanisms of TIPA to cement hydration process as seen in Fig. 3 [5, 9, 10].

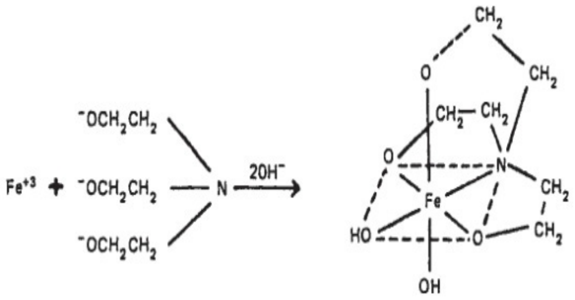

Fig. 1. Solubilization of the ferric ion in Portland Cement by TEA

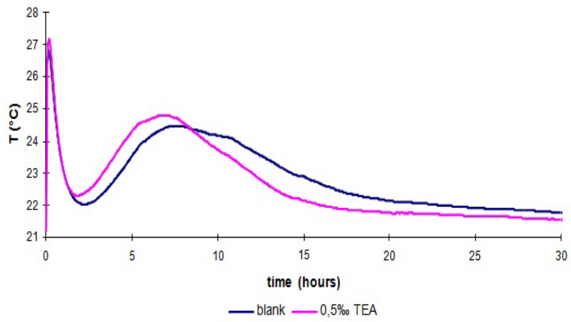

Fig. 2. Heat of hydration

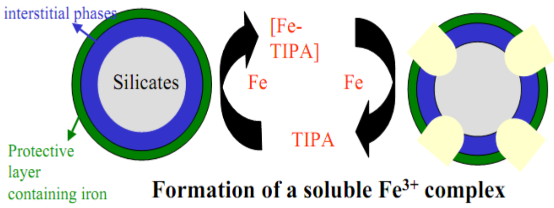

Fig. 3. Schema displaying the influence of TIPA with ferrite, proposed by Gartner and Myers

TIPA can be used as a grinding aid and it is also known to be capable of complexing Fe(III) at high pH (Fig. 4 and Fig. 5). In large polyphasis clinker grains, the retardation of ferrite hydration can also block all of the other clinker phases. TIPA disrupts an Fe^{III}–rich protective layer by facilitated Fe^{3+} transport, so the other minerals in the clinker can be hydrated earlier.

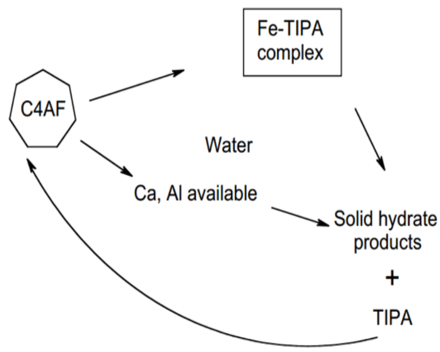

Fig. 4. complexation Fe3+ - TIPA from C4AF

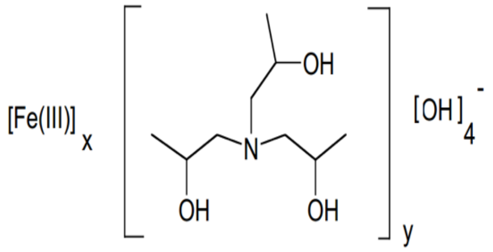

Fig. 5. The structure of the complex Fe(III)-TIPA

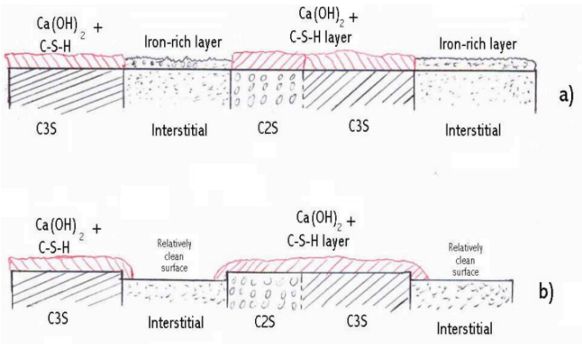

Fig. 6. Hydration process of cement with (b) and without additives TIPA (a)

Hydration process of cement with and without TIPA is described as seen in Fig. 6:

The surface of the cement particles includes C_3S, C_2S, C_3A and C_4AF minerals, in which components are mainly C_3S, C_2S; C_3A, C_4AF are called interlacing mineral. During hydration, the surface of CSH and $Ca(OH)_2$ hydration products covers the surface of C_3S, C_2S minerals and it slows down the hydration process. On the surface of interlacing mineral (C_3A, C_4AF) was similarly covered by a iron rich layer.

Without TIPA, the silicate phase is blocked by iron hydroxide. TIPA solubilizes Fe beyond sulfate depletion. removing hydrate barriers, opening up more paths for silicate hydration. TIPA solubilizes iron even after sulfate depletion [1]. Presence of the three bulky methyl groups ($-CH_3$) in TIPA provides steric hindrance that minimizes adsorption of TIPA on the hydration products [8]. This allows the facilitated iron transport to continue beyond the sulfate depletion point to speed up the mineral hydration, thus increase the strength of cement stone. This is the mechanism affecting the rate of hydration of cement mineral additives in TIPA.

According to the action mechanism of TIPA, creating complex Fe(III)-TIPA is the main principle. On the other hand, according to the research of Kevin J.Fraser, additives adding mode does not affect the cement hydration process [4].

The addition of small amounts of TIPA can result in a significant increase in the strength of cement pastes at early and late ages [7, 11]. The strength at the early ages (1 day and 3 days) of cement prepared with TEA increases, but at the age of 28 days the strength decreases. Cement prepared with TIPA, strength at 7, 28 days increases [5, 6]. This work investigated the effect of the amount and the ratio of TIPA and TEA on some properties of Portland cement.

2. Experimental Study

2.1. Materials

2.1.1. Portland cement clinker

In the research, we used clinker of Hoang Mai cement factory. Portland cement clinker was ground with gypsum in laboratory mill to produce Portland cement. Chemical and mineral compositions of clinker cement used are shown in Table 1.

Table 1. Chemical and mineral composition of clinker cement

Chemical composition (% by mass)		Mineral composition (% by mass)	
CaO	66.2	C_3S	61.98
SiO_2	21.9	C_2S	15.62
Al_2O_3	5.3	C_3A	8.28
Fe_2O_3	3.4	C_4AF	10.34
MgO	2.13		
SO_3	0.2		
K_2O	0.77		
Na_2O	0.1		

2.1.2. Lao gypsum

Lao gypsum is an opaque shape, white, and pure. The properties of Lao gypsum are shown in Table 2.

Table 2. The properties of Lao gypsum

SO_3 content (%)	39.62
Humidity (%)	2.0
Insoluble residue content (%)	3.5

2.1.3. Triisopropanolamine

Triisopropanolamine (TIPA) is an aminoalcohol which belongs to the alkanolamine group. TIPA consists of hydroxyl and amino functional groups, as seen in Fig. 7.

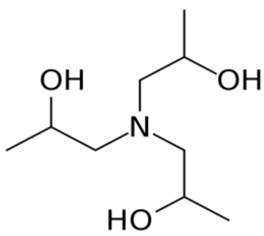

Fig. 7. Chemical structure of triisopropanolamine (TIPA) [9, 10]

TIPA is a low freeze grade variation of TIPA for easier handling in colder ambient temperatures (freezing point: 5 ºC/41 ºF). It is a blend of 85% TIPA and 15% deionized water.

Typical physical properties of TIPA are shown in Table 3.

Table 3. The properties of TIPA

Formula	$[CH_3CH(OH)CH_2]_3N$
Molecular Weight	191.27
Specific Gravity at 25/4 °C	1.027 g/cm^3
Boiling Point, °C (°F) at 760 mm Hg	104 (219)
Freezing Point, °C (°F)	5 (41)
Viscosity, cps	
At 25°C	240
At 60°C	25
Physical Form	Liquid

2.1.4. Triethanolamine (TEA)

Triethanolamine, or TEA is a viscous organic compound that is both a tertiary amine and a triol. A triol is a molecule with three alcohol groups, as seen in Fig. 8.

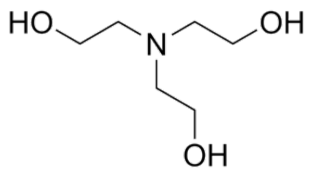

Fig. 8. Chemical structure of Triethanolamine (TEA)

Typical physical properties of TEA are shown in Table 4.

2.1.5. Sand

Sand used in this work is standard sand according to TCVN 6227:1996). Sand is packed into plastic bags weighing 1350 ± 5g and stored in cartons.

Table 4. The properties of TEA

Formula	$[CH_2(OH)CH_2]_3N$
Molecular Weight	149.19
Density (g/ml)	1.124
Boiling Point, °C (°F)	335.4 (635.72)
Melting Point, °C (°F)	21.6 (70.88)
Physical Form	Liquid

Table 5. Sand grain distribution

Sieve size (mm)	Sieve residue (%)
2	0
1.6	7 ± 5
1	33 ± 5
0.5	67 ± 5
0.16	87 ± 5
0.08	99 ± 1

2.2. Experiment

Clinker was crushed to the appropriate particle size in a hammer crusher, then it was screened carefully through a 5 mm sieve, the particle size under 1 mm was removed. Before pouring into a 500 ml beaker with water (the additives/water ratio of 1/9) and stirring for 15 minutes, the additives were taken according to the calculated ratio. Then this mixture and 3 kg clinker were taken into the ball mill. After grinding the mix for a period of 30 minutes, we obtained product as required, known as cement mix additives.

In order to determine the properties of cement with the addition of TIPA and TEA, the samples were prepared with the mixture of additives (TIPA and TEA). Table 6 represents the mix proportions for different samples.

Table 6: Mix proportion of the samples

No	Sample	Additive			
		TEA (%)	TIPA (%)	Additive/cement (%)	TEA : TIPA
1	HH0	0	0	0.000	0:0
2	HH1	0.020	0	0.020	1:0
3	HH2	0.020	0.005	0.025	4:1
4	HH3	0.020	0.010	0.030	4:2
5	HH4	0.020	0.015	0.035	4:3

In this table, the samples HH2, HH3, HH4 are cement samples mixed with two additives TIPA and TEA, the sample HH0 is ordinary cement sample used for comparison in the study, the sample HH1 is a cement sample mixed with TEA additive.

2.3. Method

Cement physical properties were determined by standard methods:

TCVN 4030 : 2003, method for determination of fineness of cement powder.

TCVN 6017 : 1995 ISO 9597 : 1989, method for determination of setting time.

TCVN 6016 : 1995 ISO 679 : 1989, method for determination of strength.

3. Results and Discussion

3.1. The Effect of TIPA and TEA on the Fineness of Portland Cement

The results of the effect of TIPA and TEA on the fineness of Portland cement are shown in Table 7. The change of fineness is shown in Fig. 9.

From the results in Table 7 and Fig. 9, we can see that cement with additives samples were finer than the ordinary cement (2503cm^2/g), the fineness of the samples HH2, HH3, HH4 (cement with TIPA and TEA) was higher than that of the sample HH1 (cement prepared with TEA).

Table 7. The effect of TIPA and TEA on the fineness of Portland cement

Sample	HH0	HH1	HH2	HH3	HH4
TEA (%)	0	0.020	0.020	0.020	0.020
TIPA (%)	0	0	0.005	0.010	0.015
Blaine (cm^2/g)	2503	2601	2613	2649	2589

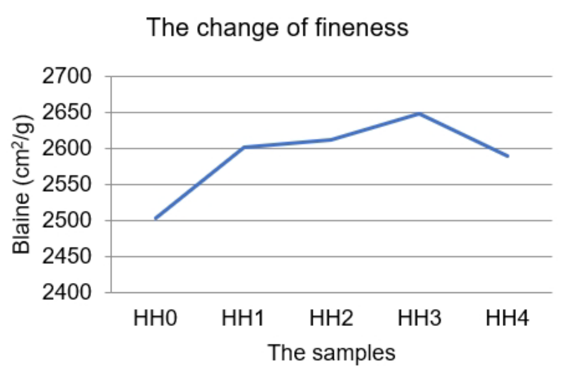

Fig. 9. The change of fineness.

The fineness of the cement increased when the TIPA content of the additive mixture increased from 0.005 to 0.01% (the highest fineness was 2649 cm^2/g of HH3 (0.01% TIPA + 0.02% TEA). When the amount of TIPA in the mixed additive continued to rise to 0.015%, the fineness of the cement reduced to 2589 cm^2/g but still finer than that of the ordinary cement. Thus, the TIPA, TEA mix admixture has an appropriate effect to increase the fineness of grinding cement. This also means the grinding efficiency of cement was improved in the cement production technology.

3.2. The Effect of TIPA and TEA on the Consistency and the Setting Time of Portland Cement

The results of the consistency and the setting time of cement are shown in Table 8 and Fig. 10.

It can be seen from the results in Table 8 and Fig.10 that the consistency of samples with additives is not different from that of ordinary cement, although the consistency tended to increase with higher amounts of additives. The initial set and final set of the samples are lower than that of ordinary cement and tend to decrease as cement added additives. This can be explained that the standard water content of the cement samples increases, this result is suitable with the result of fineness test in part 1. The higher the fineness, the higher consistency. The initial set and final set of the samples containing additives tend to decrease when the content of additives increases.

3.3. The Effect of TIPA and TEA on the Strength of Portland Cement

The effect of TIPA and TEA on the strength of Portland cement is shown in Table 9. The change of strength (R_f: flexural strength, R_c: compressive strength) is shown in Table 10. The degree of compressive strength variation is shown in Fig. 11.

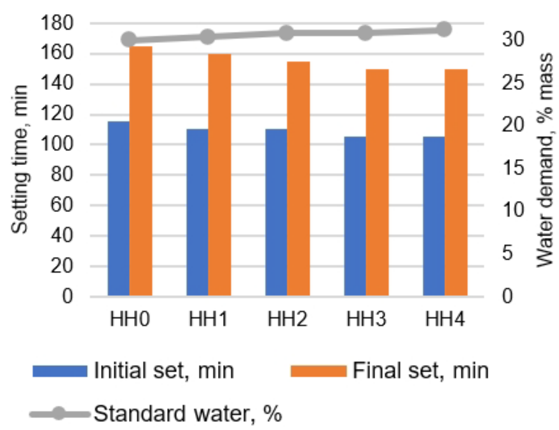

Fig. 10. The consistency and the setting time of cement

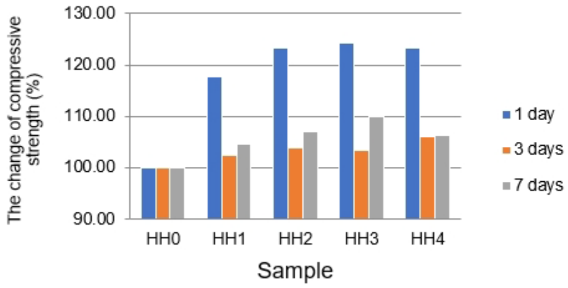

Fig. 11. The degree of compressive strength variation

According to the results in Table 9, Table 10 and Fig. 11, the compressive strength at the age of 1 day, 3 days and 7 days increased. The compressive strength at the age of 1 day (sample HH3 with 0.01% TIPA + 0.02% TEA) is the highest with an increase of 24.21%. The flexural strength and compressive strength of the mixed admixture samples (containing TIPA + TEA) are higher than that of the single admixture sample HH1 (0.02% TEA).

Table 8: The consistency and the setting time of cement

Sample	TEA (%)	TIPA (%)	Standard water (%)	Setting time	
				Initial set (min)	Final set (min)
HH0	0	0	30	115	165
HH1	0.020	0	30.4	110	160
HH2	0.020	0.005	30.8	110	155
HH3	0.020	0.010	30.8	105	150
HH4	0.020	0.015	31.2	105	150

Table 9: The effect of TIPA and TEA on the strength of Portland cement

Sample	TEA (%)	TIPA (%)	Strength (MPa)					
			1 day		3 days		7 days	
			R_f	R_c	R_f	R_c	R_f	R_c
HH0	0	0	3.92	14.87	7.05	31.00	8.73	37.20
HH1	0.02	0	5.14	17.50	7.07	31.73	8.29	38.93
HH2	0.02	0.005	5.00	18.33	7.27	32.16	7.78	39.80
HH3	0.02	0.010	5.37	18.47	7.48	32.07	8.12	40.87
HH4	0.02	0.015	5.38	18.33	7.27	32.87	8.18	39.53

Table 10: The change of the strength

Sample	TEA (%)	TIPA (%)	The change Δ (%)					
			1 day		3 days		7 days	
			R_f	R_c	R_f	R_c	R_f	R_c
HH0	0	0	100	100	100	100	100	100
HH1	0.02	0	131.12	117.69	100.28	102.35	94.96	104.65
HH2	0.02	0.005	127.55	123.27	103.12	103.74	89.12	106.99
HH3	0.02	0.010	136.99	124.21	106.10	103.45	93.01	10987
HH4	0.02	0.015	137.24	123.27	103.12	106.03	93.70	106.26

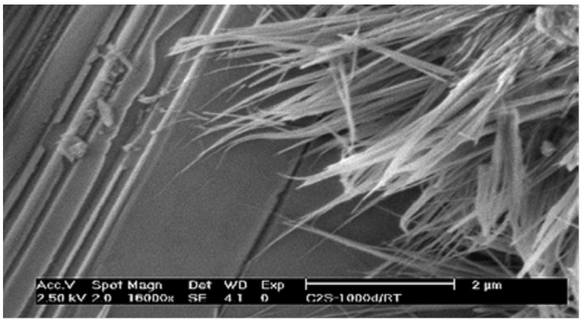

Fig. 1. The production CSH of the C_2S - hydration in cement.

We know that two additives TEA and TIPA do not have a chemical reaction. The useful properties are still expressed by combining them. The fineness of the mixed additive samples was higher than the ordinary samples. On the other hand, TIPA also speeds up hydration at 7 days of age. Therefore, compressive strength of the mixed additive samples increased when compared to the ordinary sample.

Fig. 12 illustrates the production CSH of the hydration of C_2S in cement, one of the main minerals that improve the properties of cement (standard water content, setting time, strength of cement). This hydration depends on the crystalline structure of the mineral, the amount of water, and the reaction conditions, the effect of the additive, the amounts of additives used in the cement technology [11,12].

4. Conclusion

This study showed the results of the influence of TIPA and TEA on the fineness, consistency, setting time, and strength of cement. Cement prepared with TIPA and TEA (at appropriate proportions) was higher fineness than TEA single-component cement and ordinary cement (2503 cm^2/g). The highest fineness was 2649 cm^2/g of the cement mix additive (0.01% TIPA + 0.02% TEA). The strength tended to increase, the setting time decreased as the additive content mixes into the cement samples increase. The flexural strength and compressive strength at all ages of mixed additive cement (TIPA + TEA) samples were higher than those of the single additive cement (TEA) and ordinary cement. The highest compressive strength at 1 day was sample HH3 (0.01% TIPA + 0.02% TEA) with an increase of 24.21%.

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