# THE EFFECT OF TRIETHANOLAMINE AND LIMESTONE POWDER ON STRENGTH DEVELOPMENT AND FORMATION OF HARDENED PORTLAND CEMENT STRUCTURE

Nguyen Nhu QUY [(1)] and Nguyen Trong LAM [(2)]

## SUMMARY

The presence of finely ground limestone powder in concrete becomes more and more popular due to its ability to upgrade several properties of concrete. When the limestone powder(LP) is used in concrete in combination with triethanolamine (TEA) as an accelerator the hydration and hardening process of Portland cement is likely changed. This study reported the results of the authors' research on the effect of TEA and limestone powder on strength development of concrete with varying water-cement ratio using statistic design of experiments. The results of SEM and X-ray examination reveal that TEA has a rather profound influence on the concrete strength development as well as the formation of hardened Portland cement structure.

***Keywords:*** *Accelerator, Fine filler, Strength development, Hardened cement structure.*

## INTRODUCTION

TEA is a surface active substance which is absorbed on surface of cement particles and cement hydrated products. TEA enables the solution of some metallic ion like $Fe^{3+}$ and $Al^{3+}$ thus increases the activity of $C_4AF$ compound and inhibits the formation of $Fe(OH)_3$ and $Al(OH)_3$ on surface of cement particle. This action can facilitate the hydration rate of silicate and alumilate phases in cement particle. Besides, TEA can also reduce to some extort the surface tension of water that enables the cement powder wetting and dissolving highly reactive cement compounds. In the cement paste ground limestone powder acts as fine filler and effects the formation and growth of cement hydration products. $CaCO_3$ particles act as embryos of crystallization which accelerates the hardening process as well as the formation of $Ca(OH)_2$ crystals. An attempt has been made to combine TEA and ground limestone powder together to form a chemical admixture in terms of an effective non-corroding accelerator

[1] *Ph.D, Hanoi University of Civil Engineering, email: nnquy@hotmail.com*
[2] *Eng., Hanoi University of Civil Engineering, email: laam_44vl@yahoo.com*

which doesn't adverse 28 day compressive strength. In this research the statistic design of experiments was used to investigate the influence of TEA concentration, ground limestone powder addition rate and water-cement ration on the concrete strength development as well as the formation of hardened cement paste structure.

## MATERIALS AND METHOD OF TESTING

### Materials

In this research Portland cement PC-40 produced by Chin-Fon cement plant was used. This cement is similar to cement Type I according to ASTM - C150. Oxide composition of cement is given in table 1. Normal river sand and a crushed stone were used as aggregate, their physical properties are shown in table 2 and table 3.

Table 1 Oxide composition of cement and ground limestone

| Oxide | Cement | Ground limestone powder |
|---|---|---|
| $SiO_2$ | 21,8 | 0,18 |
| $Al_2O_3$ | 6,0 | 0,30 |
| $Fe_2O_3$ | 3,3 | 0,12 |
| CaO | 64,3 | 54,20 |
| MgO | 0,80 | 0,91 |
| MnO | 0,02 | - |
| $TiO_2$ | 0,25 | - |
| $K_2O$ | 0,74 | 0,09 |
| $Na_2O$ | 0,08 | 0,06 |
| $SO_3$ | 2,4 | 0,03 |
| $Cl^-$ | 0,008 | - |
| Fr.CaO | 0,8 | - |
| L.O.I | 1,0 | 43,9 |

TEA of density $\rho$ = 1,124 g/ml and ground limestone powder with total content of $CaCO_3$ and $MgCO_3$ equal to 99,6%, fineness as 4,1% retaining on 0,08 mm sieve were used. The oxide composition of ground limestone powder is listed in table 1.

Table 2 Particle gradation of aggregate

| Aggregate type | Percentage passing through sieve size (mm) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 40 | 20 | 10 | 5,0 | 2,5 | 1,25 | 0,63 | 0,315 | 0,14 | < 0,14 |
| Sand | - | - | - | 100 | 88 | 76 | 54 | 20 | 1,9 | - |
| Gravel | - | 100 | 30 | 0 | - | - | - | - | - | - |

Table 3 Physical properties of aggregate

| Aggregate type | Specific gravity ($g/cm^3$) | Water absorption, (%) | Fineness modulus | Dry-rodded unit weight, ($g/cm^3$) | Void ration, (%) |
|---|---|---|---|---|---|
| Sand | 2,65 | 0,4 | 2,5 | 1,63 | 38,5 |
| Gravel | 2,7 | 0,2 | - | 1,62 | 40 |

**Method of testing**

Testing has been done according to the following sequence.

+ Building plan of experiments.
+ Concrete mix proportioning followed plan of experiments.
+ Study the influence of TEA and LP on cement setting time.
+ Study the influence of TEA and LP on cement hardened paste structure.
+ Study the influence of TEA and LP on concrete strength development.

The concrete mix proportions of control specimens and the optimum specimens are listed in table 4. In this paper only most successful specimens are show, as a result of statistic design of experiments with two level three factorial control composite design method.

Table 4 Concrete mix proportions

| Type of specimens | W/C | Dosage of TEA (ml/l) | Rate of LP addition (%) | Unit content, $kg/m^3$ | | | |
|---|---|---|---|---|---|---|---|
| | | | | Cement | Sand | Gavel | Water |
| Control | 0,5 | - | - | 431 | 706 | 975 | 216 |
| Test | 0,5 | 1,2 | 7,0 | 400 | 706 | 975 | 216 |

The consistency of fresh concrete mix is approximate 7,0 cm.

## RESULT AND DISCUSSION

### Influence of TEA and LP on cement setting time

Test results show that initial and final setting time of sample containing LP are shortened, but the time interval remains nearly unchanged (see figure 1). In case of samples containing TEA the initial set is delayed but the final set remains the same as for control sample (see figure 2). The combination of TEA and LP has strong effect on setting characteristics of paste. Both initial and final sets are delayed but setting time interval is shortened considerable (figure 3).

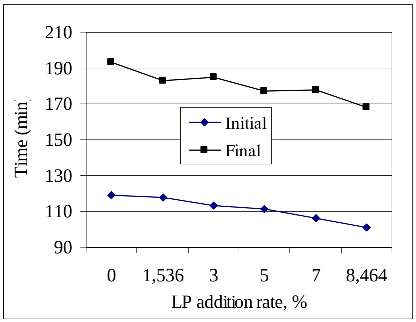



Figure1 With LP

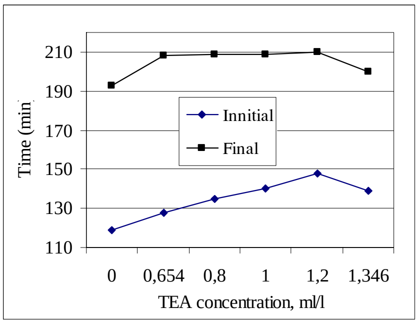



Figure2 With TEA

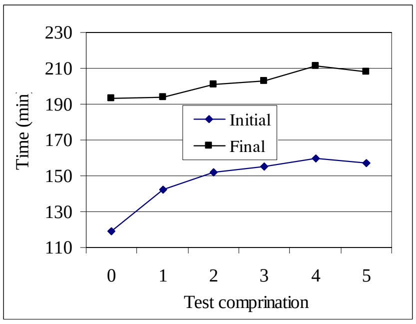



Figure3 With both TEA and LP

### Influence of TEA and LP on the concrete strength development

Test results show that the presence of TEA and LP in concrete mix accelerates its strength development (see table 5). At 3 day age the compressive strength, increases about 26% over that of control specimens. At 7 day age the increase in the compressive strength reaches up to 18%. At 28 day age the compressive strength of both tested and control specimens is nearly the same unlike the case when LP is used as fine filler alone where the 28 day compressive strength of concrete is reduced by about 10 to 20%.

Table 5 The compressive strength development of concrete

| Type of specimens | W/C | Dosage of TEA(ml/l) | Rate of LP addition | Slump (cm) | Compressive strength MPa, at the age of | | |
|---|---|---|---|---|---|---|---|
| | | | | | 3 days | 7 days | 28 days |
| Control | 0.5 | - | - | 7.0 | 28.7 | 36.0 | 47.1 |
| Test | 0.5 | 1.2 | 7.0 | 7.0 | 36.2 | 42.5 | 48.1 |

### Influence of TEA and LP on the microstructure of hardened cement paste

The microstructure of hardened cement paste with and without TEA and LP was examined by XPD and SEM. The amount of $Ca(OH)_2$ which is represented by peak with d-values 4.92, 2.63 and 1.93A$^o$.

In the samples with TEA and LP is much less than that in the control samples. This may gives an evidence of the formation of hydrates with high $CaO:SiO_2$ ratio. By 28 days the amount of $Ca(OH)_2$ crystal becomes larger in the sample with TEA and LP (see figure4, figure5, figure6 and figure7).

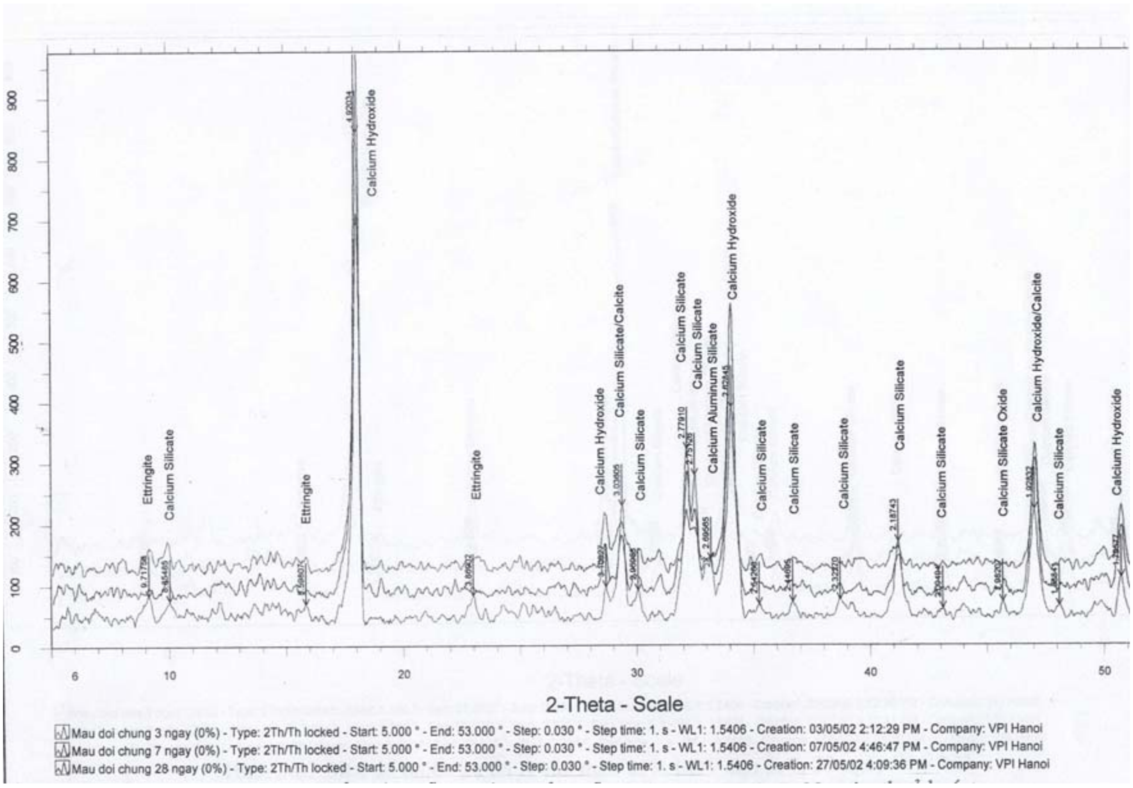



Figure 4 XPD pattern of cement paste without TEA and LP at 3, 7 and 28 days

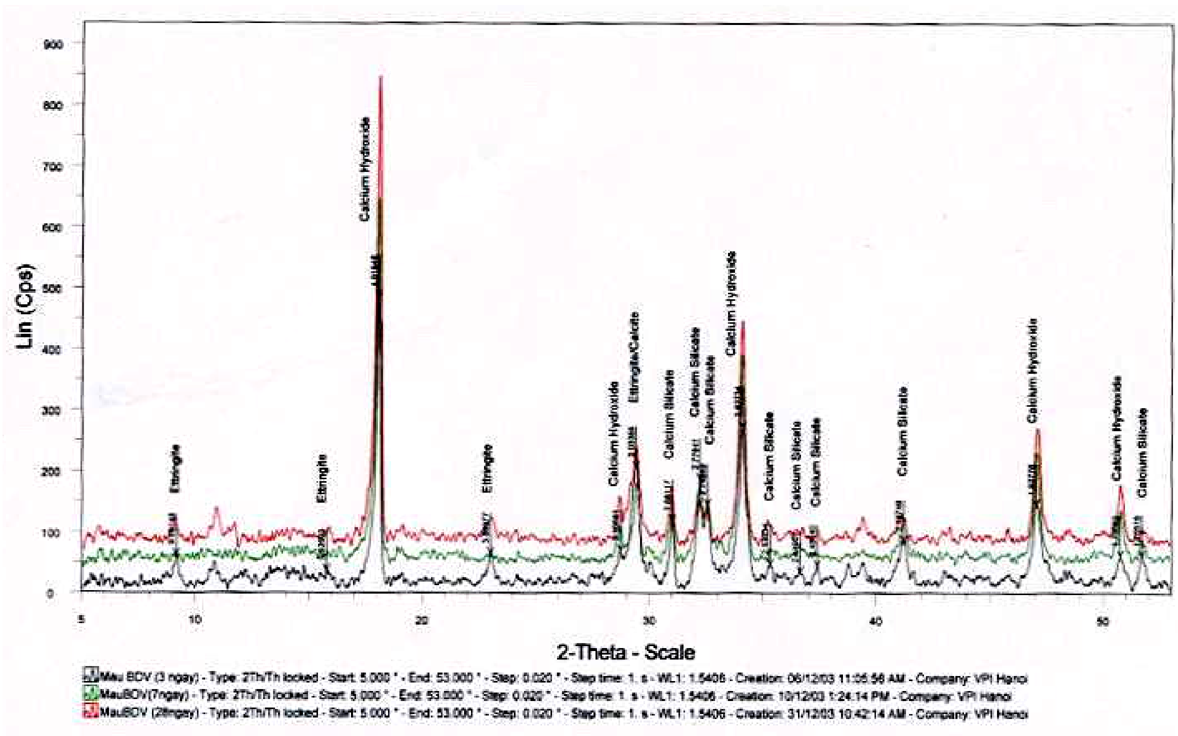



Figure 5 XPD pattern of cement paste without TEA and LP at 3, 7 and 28 days

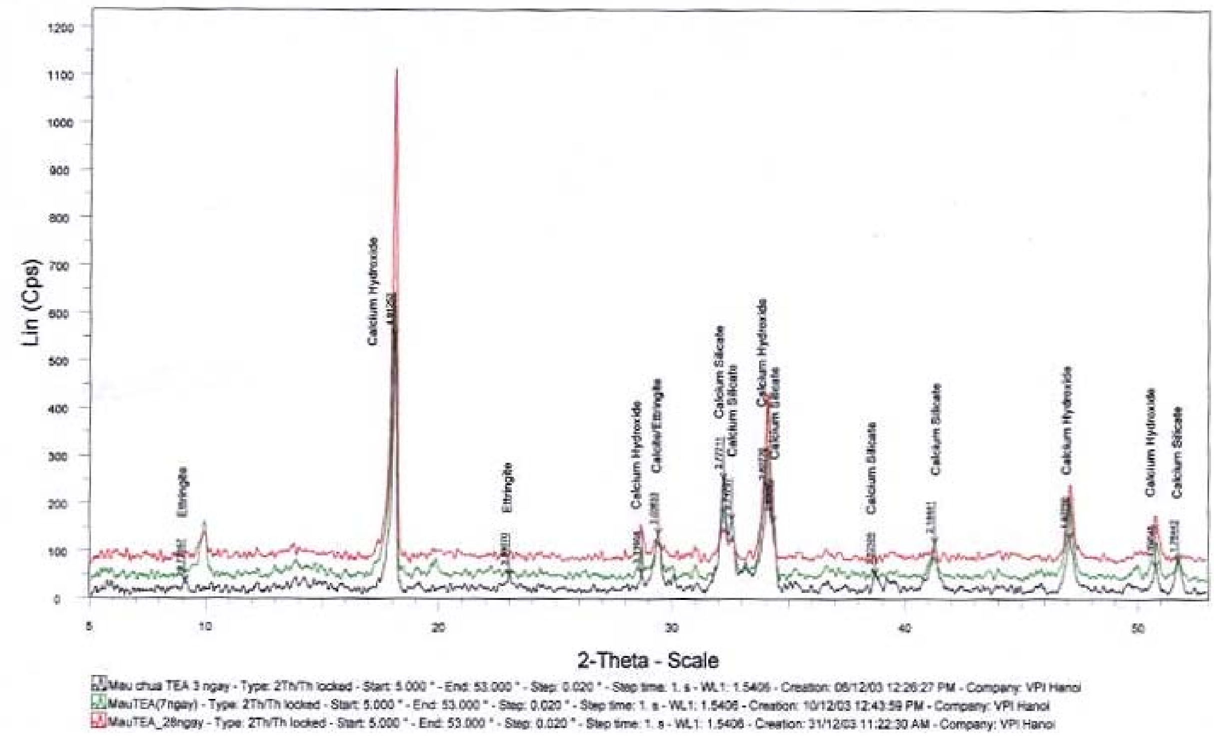



Figure 6 XPD pattern of cement paste with TEA at 3, 7 and 28 days

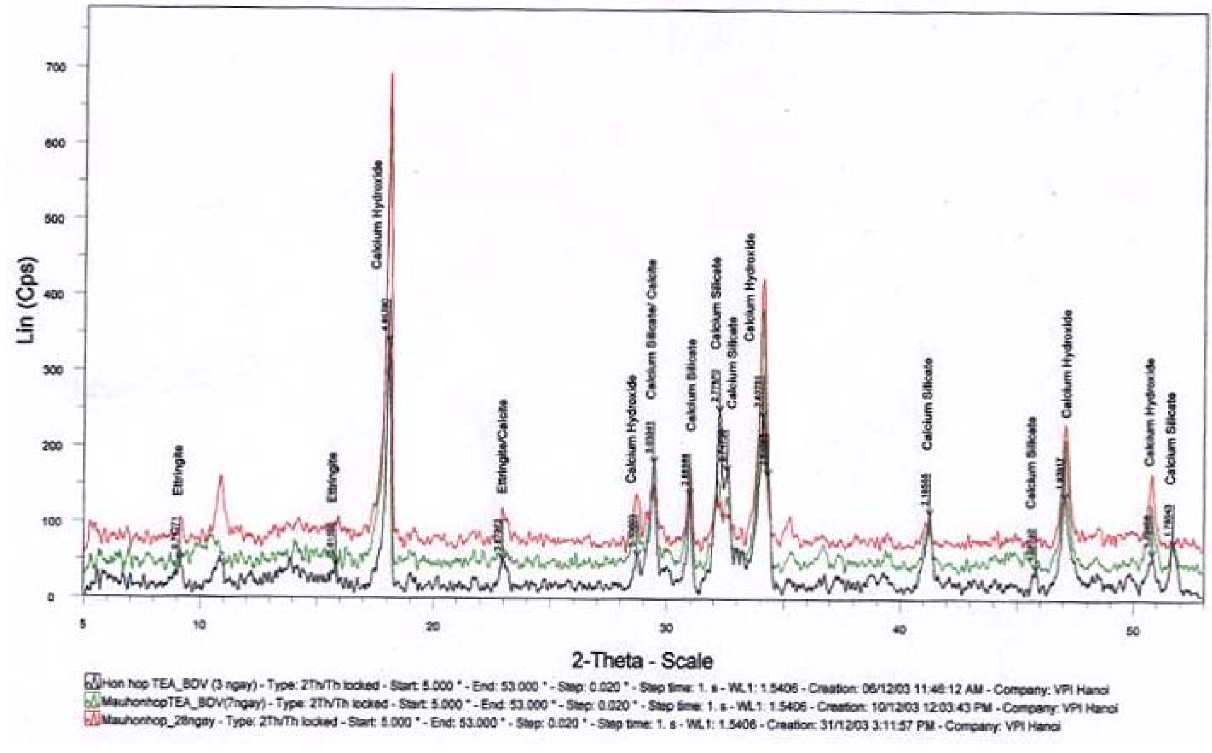
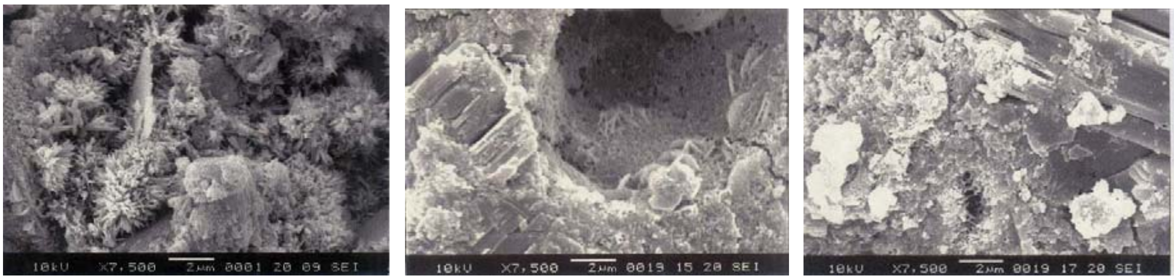



Figure 7 XPD pattern of cement paste with TEA and LP at 3, 7 and 28 days

The microphotographs (see figure8, figure9, figure10 and figure11) show clear difference in microstructure of hardened cement paste with and without TEA and LP.

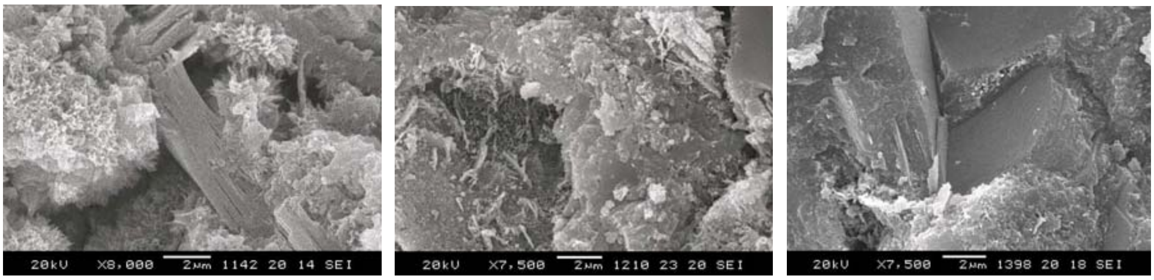


At 3 days At 7 days At 28 days

Figure 8 SEM image of cement paste without TEA and LP at 3, 7 & 28 days

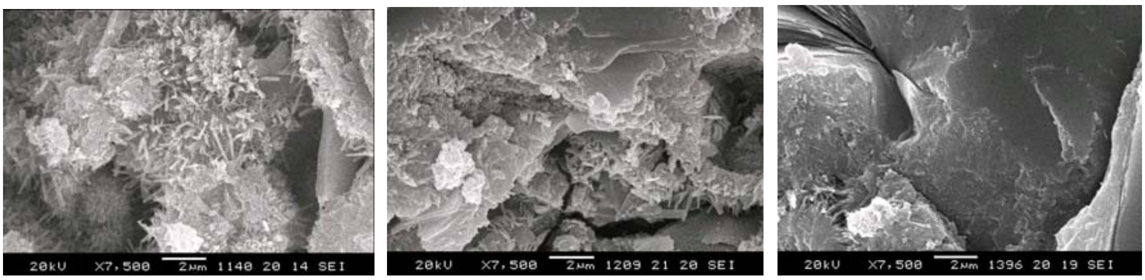
At 3 days At 7 days At 28 days

Figure 9 SEM image of cement paste with LP at 3, 7 & 28 days



At 3 days At 7 days At 28 days

Figure 10 SEM image of cement paste with TEA at 3, 7 & 28 days



At 3 days At 7 days At 28 days

Figure 11 SEM image of cement paste with TEA and LP at 3, 7 & 28 days

After 3 days hydration the sample containing 7% LP show a large quantity of Ettringite of coarse crystallization distribute in large pores. These ettringite crystals may increase the density of hardened cement paste. In the sample with TEA a large amount of hydrates filling up the space between cement particles. These hydrates crystallized in form of coarse flakes. In the samples with both TEA and LP apart from a large quantify of hydrates the ettringite crystals are also presented. In these samples the coarse hydrates in form of plats are also observed. In later period of hydration the differences in the hardened cement microstructure can hardly be observe more over the hardened cement paste with TEA and LP is seem to be denser.

## CONCLUSIONS

Within tested material combination the following conclusion can be drawled:

1. The presence of TEA and LP shortens the time interval between initial and final setting time of cement paste.
2. With dosage of 7% LP and TEA concentration of 1.2 ml/l the combination admixture accelerates the concrete strength development in early stage hydration and eliminates the strength reduction of concrete at 28 days of hydration which is common for concrete with LP addition alone.
3. XPD and SEM examination show visible change in Ettringite crystals' morphology and the combination o TEA and LP accelerates cement hydration thus increases its density

## REFERENCES


1. Nguyen Nhu Quy, "Study into the use of TEA as non-corroding accelerator for concrete". PhD thesis, Ha Noi University of Civil engineering, 1997.
2. Nguyen Nhu Quy, "Development and production of self compacting concrete using vocally available materials in Viet Nam", project assigned by the Ministry of Education and Training, 2003.
3. Ramachandran, V.S., "Action of Triethanolamine on the Hydration of Tricalcium Aluminate" Cement and Concrete Research, Vol.3, 1973, pp. 41-54
4. Ramachandran, V.S., "Hydration of Cement - Role of Triethanolamine" Cement and Concrete Research, Vol.6, 1976, pp. 623-632.
5. Rixom, M.R., "Chemical Admixture for Concrete" E & F.N. Spon Ltd., 1986, pp. 145 - 175
6. Jean Péra, et al, "Influence of Finely Ground Limestone on Cement Hydration", Journal "Cement and Concrete Composite" 1999
7. Daimon and Sakai, E., "Limestone Powder Application" Proc. of Fifth International Symposium on Cement and Concrete Technology, Oct. 1998, Beijing, China, International Academic Publisher, Beijing.

8. Chen Yilan and Wen Ziyum, “Research on Activity of Limestone for Cement Admixture”, Proc. of Fifth International Symposium on Cement and Concrete Technology, Oct. 1998, Beijing, China, International Academic Publisher, Beijing.
9. Stark, J. et al, “Investigation into the Influence of Limestone Additions to Portland Cement Clinker Phases on the Early phase of Hydration”, Proc. of International Conference held at the University of Dundee, Scotland, UK. on 8-10, Sept. 1999, Edited by Ravindra k. Dhir, Thomas D. Dyer
10. Li Buxin, et al., “Study on Portland Limestone Cement Performance”, Proc. of Fifth International Symposium on Cement and Concrete Technology, Oct. 1998, Beijing, China, International Academic Publisher, Beijing.