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EVALUATION OF EFFECT OF BLEND OF LIMESTONE AND GYPSUM ON THE COMPRESSIVE STRENGTH OF PORTLAND BLENDED CEMENT

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Abstract. Limestone and gypsum all affect the strength of hardened cement paste. However, for practical application in each plant, the interaction of each specific mixture of limestone and gypsum to the strength of each specific cement still needs to be further verified. This paper will focus on clarifying the mechanism of simultaneous impact of gypsum and limestone additives on compressive strength of cement.

The experimental results show that the addition of the combination of limestone and gypsum improves the compressive strength of cement when using limestone or gypsum separately. Cement samples use only 5 wt% gypsum or 5 wt% limestone as additives, with a compressive strength after 1 day reduced from 15 % to 80 % compared with cement samples using a mixture of 5 wt% gypsum and 5 wt% limestone as additives. This can be explained by the role of limestone in stabilizing of ettringite, preventing phase transformation from the AFt phase to the AFm phase.

Keywords: gypsum, limestone, blend, strength, PCB cement.

Classification numbers: 2.9.2, 2.9.4.

1. INTRODUCTION

Limestone and gypsum are two common additives in Portland cement blended (PCB). There have been many studies [1-7] on the effect of each of these additives on propreties of cement. However, in each specific case, the effect of combination of them has been still needing additional research.

The addition of gypsum has been used to control the setting time, and improving cement strength, especially early strength of cement [1, 2]. Besides, limestone has been known as a filler additive, also known as inert additive, which is mixed into cement with the purpose of increasing the capacity of cement production, and result in lowering product costs. In addition, when mixing inert additive in cement, it is necessary to pay attention to the proportion to ensure the quality of the product [1, 3].

In fact, some studies [4-7] show that limestone is not just a filler additive. It also participates in the hydration process, creating products similar to that of gypsum, contributing to improving the early strength of hardened cement paste.

This paper focuses on the interaction effect between limestone and gypsum on compressive strength of cement. The experimental results from this research reveal great practical implications for the Portland cement blended, in which it provides more useful information and references for the study of synergistic effects of gypsum and limestone additives on the development of strength of Portland cement blended.

2. MATERIALS AND RESEARCH METHODS

2.1. Materials

The materials used in the study include: FiCO Tay Ninh clinker (meet the requirements of Vietnamese standard TCVN 7024: 2013), Sroc Con Tran Tay Ninh limestone, Thailand gypsum (comply with the TCVN 9807: 2013).

The chemical and mineral composition of FiCO Tay Ninh clinker (determined according to TCVN 141:2008 and TCVN 7024:2013) is shown in Table 1. The chemical composition of Sroc Con Tran Tay Ninh limestone (determined according to TCVN 9191:2012) is shown in Table 2. The chemical composition of gypsum (determined according to TCVN 9807:2013) is shown in Table 3.

Table 1. Mineral and chemical composition of Fico Tay Ninh clinker.

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO
21.04	5.62	3.60	3.76	64.31
C_3S	C_2S	C_3A	C_4AF	
58.92	16.19	8.81	10.94	

Table 2. Chemical composition of Sroc Con Tran Tay Ninh limestone.

LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
40.38	4.82	1.29	0.37	49.95	2.44

Table 3. Chemical composition of gypsum.

LOI	SO_3	SiO_2	Al_2O_3	Fe_2O_3	CaO
20.71	45.63	0.88	0.00	0.50	32.23

2.2. Preparation of cement samples

Clinker, limestone and gypsum was crushed to a particle size smaller than 5 mm. Then, each material was ground separately in a test ball mill with the same grinding time of 65 minutes. Clinker powder, limestone powder and gypsum powder were mixed in proportion to the ingredients (Table 4) to create samples M22, T22, D22 and TD22.

2.3. Test methods

Normal consistency and setting time of cement were determined according to TCVN 6017: 2015. The fineness of cement was determined according to TCVN 4030: 2003. The strength of cement was determined according to TCVN 6016: 2011. Scanning electron microscopy (SEM) images were used to detect specific forms of minerals, microstructures, and crystals of hardened cement paste.

Table 4. Proportions of clinker, limestone and gypsum powders in this study.

Sample	Clinker, wt%	Gypsum, wt%	Limestone, wt%
M22	100	0	0
T22	95	5	0
D22	95	0	5
TD22	90	5	5

3. RESULTS AND DISCUSSION

3.1. The fineness of samples using gypsum and limestone additives

Clinker, limestone and gypsum were separately crushed, then mixed in different proportions, mixing ratio and fineness are given in Table 5.

Table 5. The Blaine fineness and residual fineness of R0.045, R0.09 sieve of cement samples.

Sample	Clinker, wt%	Gypsum, wt%	Limestone, wt%	Blaine, cm^2/g	Residual R0.045, %	Residual R0.09, %
M22	100	0	0	4286	12.74	1.39
D22	95	0	5	4391	11.23	1.01
T22	95	5	0	4141	13.53	2.89
TD22	90	5	5	4747	13.83	3.32

In which: R0.09 sieve has mesh sizes of 90 μm and R0.045 sieve has a mesh sizes of 45 μm.

Although with the same grinding time, but the grinding ability of clinker, limestone, gypsum varies, so the fineness of different mixes is also different.

3.2. Compressive strength of samples using gypsum and limestone additives

The individual effects of gypsum and limestone additives, as well as the effects of simultaneous use of limestone and gypsum additives on the compressive strength of hardened cement paste are given in Table 6.

Table 6. The compressive strength of cement samples mixed with gypsum and limestone additives.

Sample	Grinding time, min	Blaine fineness of blended cement, cm^2/g	Compressive strength, MPa			
			1 day	3 days	7 days	28 days
M22	65	4286	11.7	23.4	31.6	45.3
D22	65	4391	13.9	27.8	33.7	40.6
T22	65	4141	21.8	35.2	48.9	55.1
TD22	65	4747	25.1	36.4	46.0	54.2

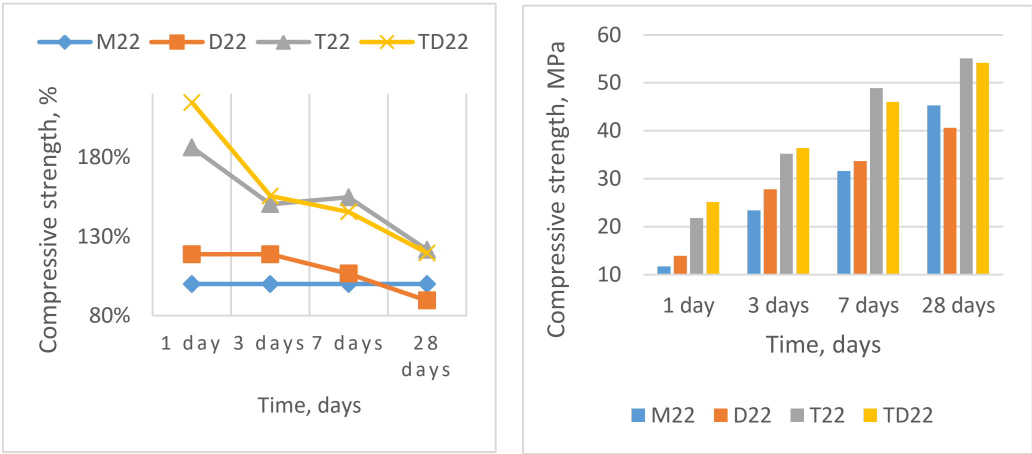

Figure 1. Compressive strength of hardened cement paste at 1, 3, 7, 28 days.

From Table 6 and Figure 1, it can be seen that:

When replacing 5 wt% of clinker by limestone, compressive strength of samples at 1, 3 and 7 days is improved, however, the compressive strength at 28 days is reduced incomparable with that of M22 sample. This result is not different from other research results [3-7]. Besides, when replacing 5 wt% of clinker with gypsum, compressive strength is improved at all days. This result is consistent with other studies [1,2].

Moreover, when replacing 10 wt% of clinker with 5 wt% of limestone and 5 wt% of gypsum, although the amount of clinker decreases, the strength of this blended cement sample is still improved in comparable with that of T22 and D22 samples.

It can be seen that the rate of increase in compressive strength decreases with time. The earlier the age is, the higher compressive strength increase. The addition of gypsum additives affects compressive strength more significantly than that of limestone additives. The simultaneous use of limestone and gypsum improves the compressive strength better than separate use.

Specifically, when using limestone (D22), gypsum (T22) and the combination of gypsum and limestone (TD22), the compressive strength after 1 day increases by 20%, over 85%, and over 110% compared with that of the original M22 cement sample, respectively. However, the increasing rate of compressive strength up to 28 days is decreased, the increase is only -10% for the D22 sample and about 20% for the T22 and TD22 samples.

3.3. Microstructure analysis of samples using gypsum and limestone additives

Scanning electron microscopy images are used to detect specific forms of minerals, microstructures, and crystals. SEM images of hardened cement paste samples, i.e. M22, D22, T22, TD22, are shown in Figure 2.

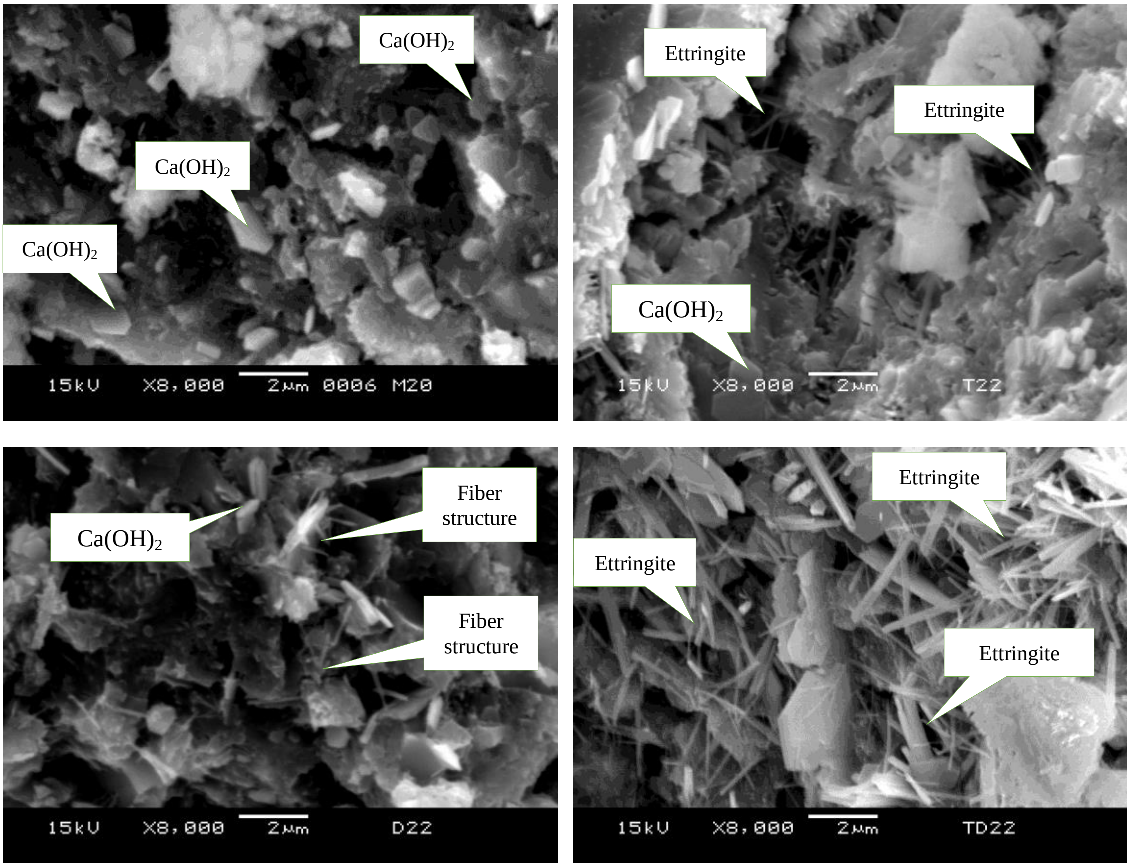

Figure 2. SEM images of M22, D22, T22, TD22 samples.

It can be observed from figure 2 that:

The $Ca(OH)_2$ hydration product mainly appears in the sample M22. With samples D22 and T22, there appear more intertwined fiber or needle structures in pores. This may be the product of $C_3A.3CaCO_3.(31\text{-}32)H_2O$ in sample D22, or the product of $C_3A.3CaSO_4.31H_2O$ (ettringite) in the T22 sample. Fibrous and needle-like structures interwoven in pores and increased bonding capacity contribute to increase compressive strength.

Moreover, ettringite crystals can be observed more clearly in the sample TD22 , but not found in samples using only limestone (D22) or only gypsum (T22). According to previous studies [1], the ettringite (AFt) phase over time will gradually shift to monosulfoaluminate (AFm) phase. At the same hydration time, the ettringite phase in the T22 and TD22 samples is significantly different. This indicates a mutual impact when adding the combination of limestone and gypsum. The addition of limestone will contribute to increase the stability of ettringite, preventing phase transformation from the AFt phase to the AFm phase. This is the main reason for the improved compressive strength of TD22 sample in comparable with that of the T22 and D22 samples, especially at early ages as the ettringite product plays an important role in the strengthening the microstructure of cement paste, and resulting in improving compressive strength of samples.

The results of the SEM image analysis (the addition of limestone will contribute to increase the stability of ettringite, preventing phase transformation from the AFt phase to the AFm phase) are completely consistent with the results of compressive strength in section 3.2.

4. CONCLUSIONS

Based on the experimental results of this study, the following conclusions can be drawn:

- The addition of limestone and gypsum additives all increases the compressive strength of hardened cement paste.

- The strength of blended cement increases with time. The earlier the age is, the higher the compressive strength increase. When using limestone (D22), gypsum (T22) and gypsum limestone (TD22), the compressive strength after 1 day is increased by 20 %, over 85 %, and over 110 % compared with that of the original M22 cement sample, respectively. However, the rate of increasing in compressive strength up to 28 days is decreased, the increase is only -10 % for the D22 sample and about 20 % for T22 and TD22 samples.

- The addition of gypsum additives influences on compressive strength of blended cement more significantly than that of limestone additives. The simultaneous use of limestone and gypsum improves compressive strength higher than it is used seperately.

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