International Journal of Science and Engineering Applications
Volume 5 Issue 7, 2016, ISSN-2319-7560 (Online)

Effects of ultrafine limestone powder on some properties of Portland cement

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Abstract: Limestone is usually ground with clinker, gypsum and mineral additives to produce blended Portland cement [2,3,4,7]. In this case, the main size of limestone is 20÷30 μm, limestone plays a role as filler. However, using ultrafine limestone powder (with the main size is about 2÷3 μm) creates many different properties, it becomes a mineral additive to increase the quality of cement. This paper presented some results about the effect of ultrafine limestone powder from Yenbai with a reasonable amount on some properties of Butson portland cement. When we used ultrafine limestone powder with a reasonable amount, the early strength of cement increases 20%; simultaneously, the bleeding of cement decreases.

Keywords: cement, additive, ultrafine limestone, properties, strength

1. INTRODUCTION

Cement production technology has a long life and has much improved compared to the past in order to improve productivity, and the quality of cement. However, two major problems in cement production is always attracted, the reduction of production cost and waste pollution. One of the effective measures to solve this problem is the use of mineral additives [7].

This paper refers to some resuls about the effect of ultrafine limestone powder on some properties of cement. The goal raised the possibility of using ultrafine limestone partially substitute clinker in cement, contribute to improve some properties of cement, simulanously, reduce CO_2 emissions from the process of cement production.

2. EXPERIMENTAL

2.1 Materials

Butson portland cement, Vietnam standard sand, Yenbai ultrafine limestone powder.

Tab. 1 shows a chemical composition of Butson portland cement.

Table 1. Chemical composition of Butson portland cement

Chemical composition (%)							
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O+Na_2O	SO_3	LOI
64,88	21,24	5,27	3,19	2,26	0,94	1,88	0,33

Tab. 2 shows particle sizes and chemical compositions of Yenbai utrafine limestone powder.

Table 2. Particle size and chemical composition of Yenbai untrafine limestone powder

Particle size (%/μm)					
%<	10	25	50	75	90
μm	0,545	0,773	1,871	3,040	4,834
Chemical composition (%)					
LOI	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO
43,53	0,18	0,009	0,039	54,98	0,5

2.2 Methods

Some physical properties: TCVN.

Structural characteristics, composition phase/mineral: SEM, DTA, XRD.

To determine the particle sizes of 0,4 ÷ 2000 μm: equipment use 750 nm wavelength laser source by light scattering principle.

3. RESULTS AND DISCUSSION

3.1 Effect of ultrafine limestone powder on some properties of cement (consistent, setting time, spread and bleeding, strength)

The influence of addition of ultrafine limestone powder (UL) to the Portland cement was determined through the examination of consistent, setting time, spread and bleeding, strength is shown in Tab. 3.

Table 3. Effect of ultrafine limestone powder (UL) on some properties of cement

Sample	UL (% mass)	Water demand (% mass)	Setting time (min)		Water/Cement	Spread (mm)	Water/Rigid	Bleeding (%)
			Initial	Final				
S0	0	27,20	96	150	0,5	86,25	0,9	16,01
S5	5	26,00	55	115	0,5	79,00	0,9	12,72

S10	10	26,40	52	110	0,5	63,75	0,9	5,68
S15	15	26,80	45	94	0,5	53,50	0,9	3,22
S20	20	26,80	40	104	0,5	59,38	0,9	2,03
S25	25	28,00	35	98	0,5	58,13	0,9	1,16
S30	30	29,20	44	90	0,5	46,63	0,9	1,17
S35	35	29,60	37	93	0,5	51,38	0,9	0,56

3.1.1 Normal consistency

The water requirement, determined on the fresh paste, is reported in Tab. 3. It seems that utrafine limestone powder reduces water requirement compared to Portland cement. Moreover, increasing the amount of limestone requires much water.

3.1.2 Setting time

From Tab. 3, it indicates the initial and final setting time of cement pastes at different amount of limestone. The obtained values show that both initial and final setting times were decreased with an increase in the amount of limestone. It can be concluded that limestone fills the pores between cement particles due to formation of carboaluminates, which may accelerate the setting of cement pastes.

3.1.3 Spread of cement paste

The results from Tab. 3 show that the spread of cement pastes was decreased. Because of using ultrafine limestone powder, with w/c = constant, caused higher specific surface area, thus the thickness of the water layer on cement particle surface decreases, which increases the internal friction, leading to reduce spread of cement paste.

3.1.4 Bleeding

When we using ultrafine limestone powder, the bleeding of cement pastes decreases. The more amount of additive, the more reduction of separated water. The amount of separated water greatly reduced in samples of 5; 10; 15% cement replacement additive (the bleeding decreased from 16% to 3,2%); then, it slowly reduced in the other ratios.

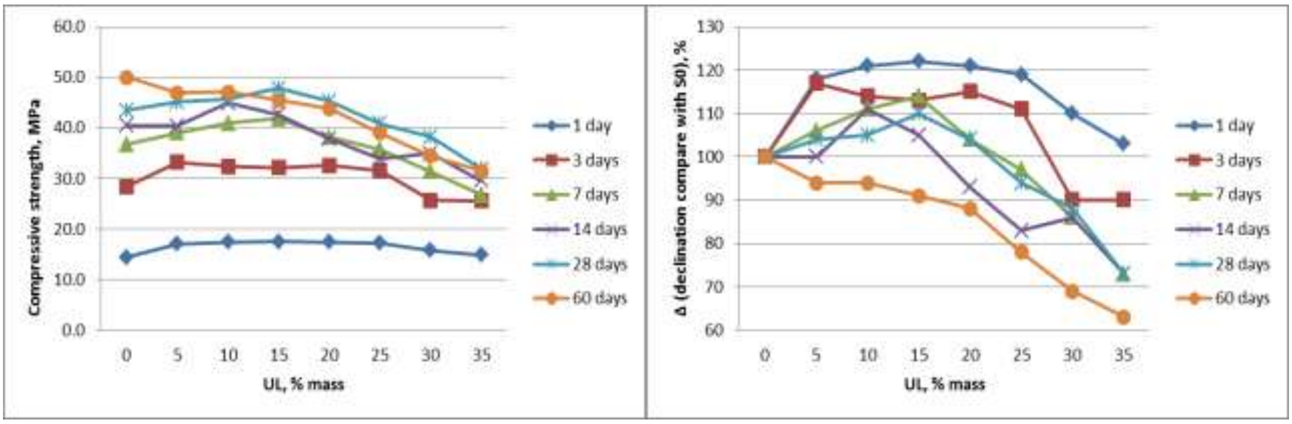
This result is caused of the ultrafine limestone particles increases the surface area, the amount of adsorbed water around the surface of the particles also increases. In contract, the formation of monocarboaluminate ($C_3A.CaCO_3.11H_2O$), hemicarboaluminate ($C_3A.0,5CaCO_3.0,5Ca(OH)_2.11,5H_2O$), which increases the water holding capacity of cement paste, so the amound of separated water decreases.

3.1.5 Strength

The influence of the ultrafine limestone powder addition on the compressive strength of cement is shown in Tab. 4 and Fig. 1.

Table 4. Effect of ultrafine limestone powder (UL) on compressive strength of cement

Sample	UL, % mass	Compressive strength, MPa						Δ (declination compare with S0), %					
		1 day	3 days	7 days	14 days	28 days	60 days	1 day	3 days	7 days	14 days	28 days	60 days
S0	0	14,4	28,4	36,7	40,5	43,5	50,0	100	100	100	100	100	100
S5	5	17,0	33,2	39,0	40,4	45,1	46,9	118	117	106	100	104	94
S10	10	17,4	32,4	40,9	44,9	45,6	47,1	121	114	111	111	105	94
S15	15	17,5	32,1	41,8	42,6	47,8	45,5	122	113	114	105	110	91
S20	20	17,4	32,6	38,2	37,8	45,3	43,8	121	115	104	93	104	88
S25	25	17,2	31,6	35,7	33,8	40,8	39,0	119	111	97	83	94	78
S30	30	15,8	25,7	31,4	34,9	38,2	34,5	110	90	86	86	88	69
S35	35	14,9	25,6	26,8	29,6	31,8	31,5	103	90	73	73	73	63



(a) Compressive strength (b) Declination

Figure 1. Effect of UL on compressive strength of cement

Tab. 4 and Fig. 1 show that:

Ultrafine limestone powder increases compressive strength at early ages (1; 3 days). Lower declination are obtained with higher addition levels.

Ultrafine limestone decreases compressive strength of cement at the later age (60 days). Higher amount of addition, lower declination.

When we use addion with amount lower 15%, the compressive strength of cement increases at early ages, decreases at later age.

This result is caused of some reasons:

Limestone improves the hydration rate of minerals C_3S, C_3A, C_4AF [7].

The presence of ultrafine limestone was slowed down the formation of C_3AH_6; simultaneously, the formation of monocarboaluminate ($C_3A.CaCO_3.11H_2O$), hemicarboaluminate ($C_3A.0,5CaCO_3.0,5Ca(OH)_2.11,5H_2O$) [1,3,4,6].

The effect of aggregate and crystalline nuclei of limestone powder is a favorable condition for the formation and development of crytalline hydrate. It gradually fills the pores between particles of cement, creates the dense structure. Moreover, with the ultrafine size, this band of limestone might contribute to improve the grain composition, arrange tightly structure and reduce the size of the pores in cement hydrated.

Increasing levels of additives cause the dilution of minerals, which reduces the intensity of cement hydrated when excessive levels of additives.

The decline in the intensity at the age of 60 days likely due to the conversion of the mineral form of ettringit to calcium monosulfoaluminate, calcium monocarboaluminate accompanying volume change (d_{ett} = 1,77 g/cm^3 < d_{mono} = 2,17 g/cm^3), also due to slowing C_3AH_6 formation, or the transformation of calcium monocarboaluminate from thin sheets to form shape metal rod will cause residual stress [6]. These changes cause the volume reduction and create pores in cement hydrated. Since then, the strength of cement hydrated tend to decrease when combined with limestone. This is usually seen in the report on the recent studies.

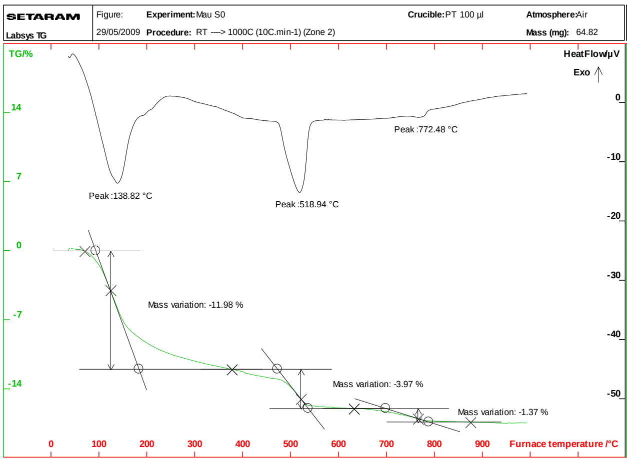
3.2 The effect of ultrafine limestone on the process of the hydration and the formation of crystals

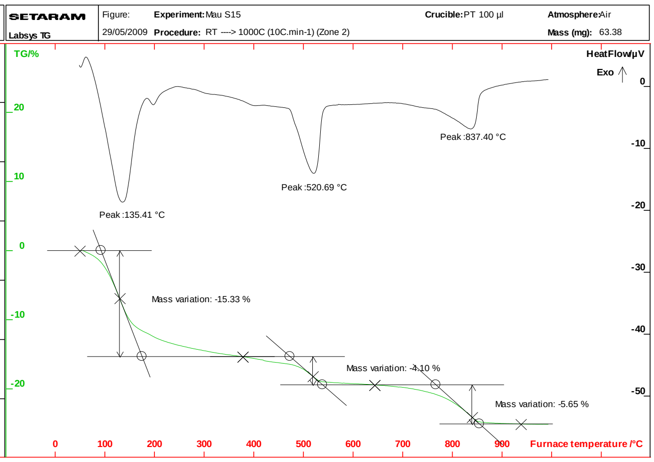
3.2.1 Differential thermal analysis (DTA)

At a temperature of less than 250ºC, the amount of loss H_2O is free water, bound water of calcium silicate hydrate CSH (B), calcium aluminate hydrate (ferrite) [5].

From 250ºC to 500ºC, the amount of water loss is mainly caused by the decomposition of $Ca(OH)_2$, and a part of the remaining calcium silicate hydrate minerals [5].

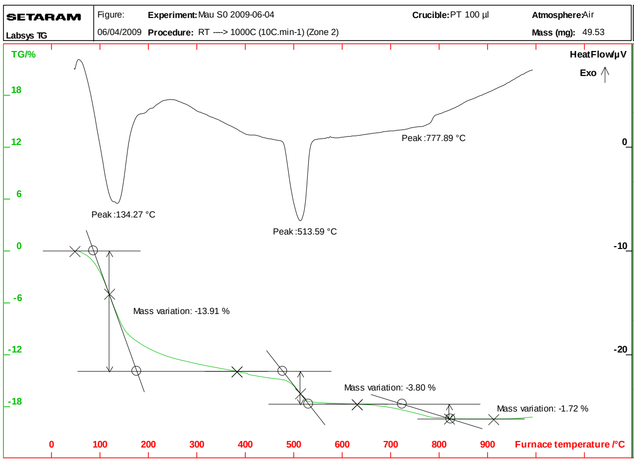
From 500ºC to 1000ºC, the amount of LOI is caused by the hydration of the remaining compounds and CO_2. CO_2 is considered to be the result of the decomposition of $CaCO_3$ in the cement hydrated; created by the reaction between $Ca(OH)_2$ and CO_2 in air and $CaCO_3$ in additives [5].

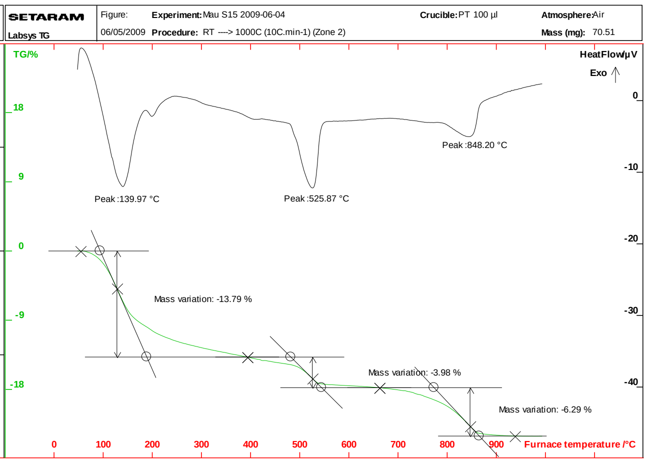




(a) DTA of S0 at 7 days

(b) DTA of S15 at 7 days





(c) DTA of S0 at 14 days

(d) DTA of S15 at 14 days

Figure 2. DTA of the samples at different ages

It is considered that LOI of cement is the loss of free water at temperatures below 100°C, and dehydration at below 500°C in the compounds of calcium silicate hydrate CSH (B), calcium aluminoferrite (ferrite) and $Ca(OH)_2$. Hence the minus can be seen as separate chemical water.

LOI of cement samples, after the ages of hydration, at the temperature below 500°C follows in table 5:

Table 5. LOI of S0 and S15

Day	LOI, %					
	S0			S15		
	<100°C	500°C	100 ÷ 500°C	<100°C	500°C	100 ÷ 500°C
7	1,2	14	12,8	2,3	17	14,7
14	2,5	15,4	12,9	1,3	15,1	13,8

It is clear that, when temperatures range from 100°C to 500°C after 7 and 14 days, the amount of losing water of S0 sample (pure cement) is less than S15 sample (cement has 15% limestone).

From DTA diagrams in Fig. 2, the weight loss in temperature ranges below 500°C of samples which have the additive is higher than pure cement samples, while the content Portland cement minerals in the samples which have the additive is smaller than test samples. The figure indicates that the additive has stimulated the process of hydration and solid, accelerated these processes.

3.2.2 XRD analysis

The results of XRD analysis are shown in Fig. 3 and Fig. 4 below:

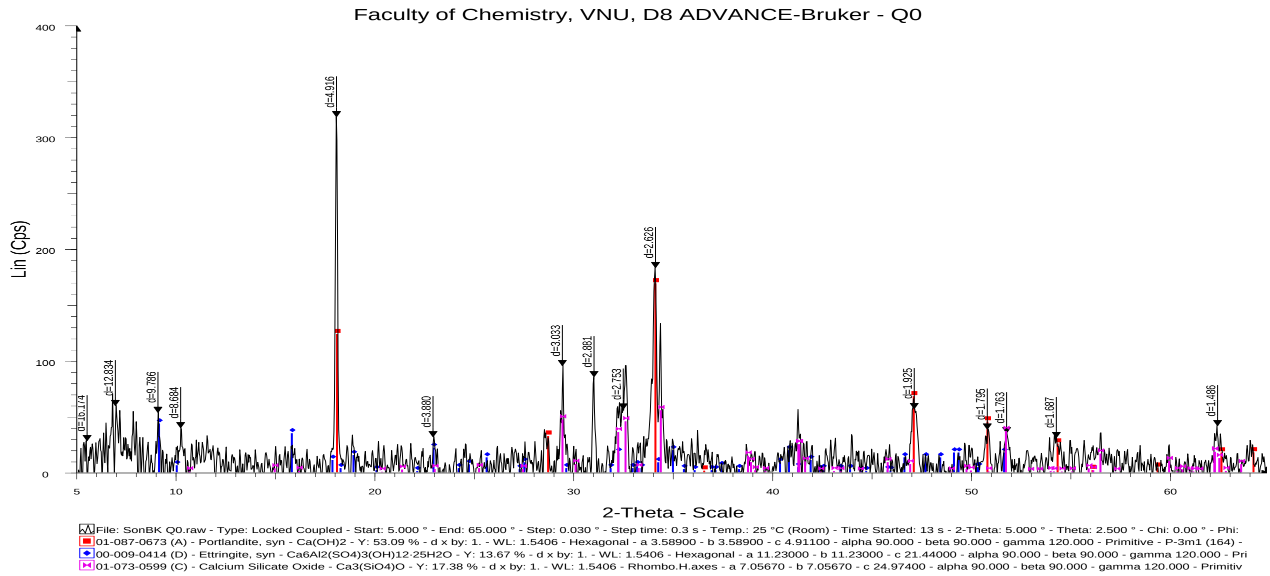


Figure 3. XRD of S0 at the age of 7 days

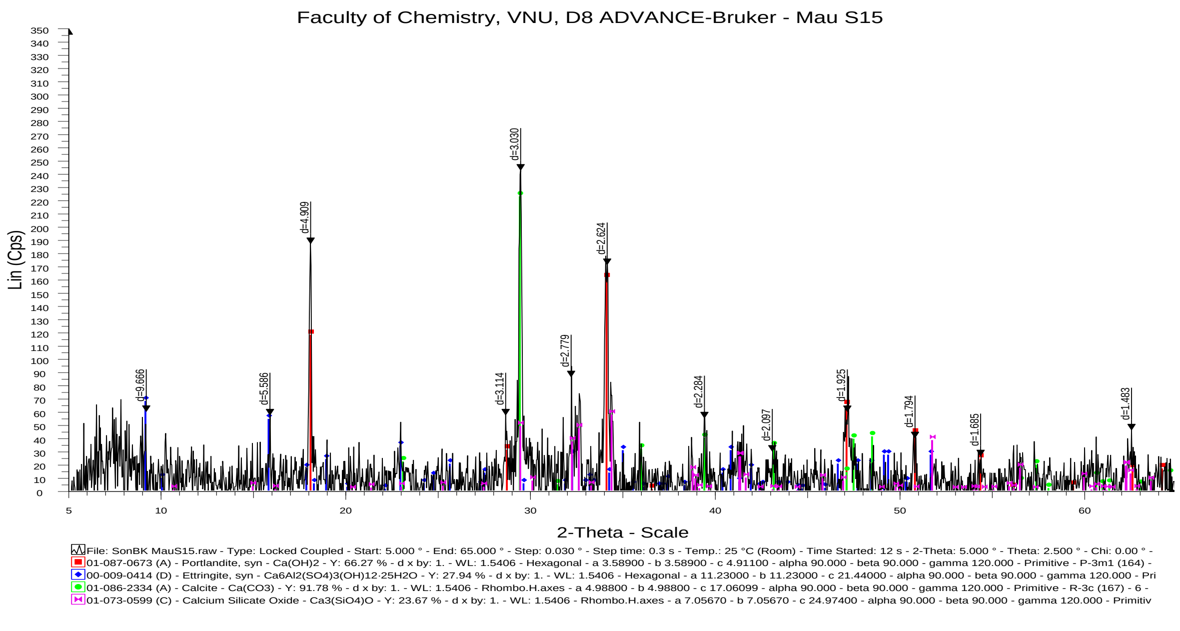
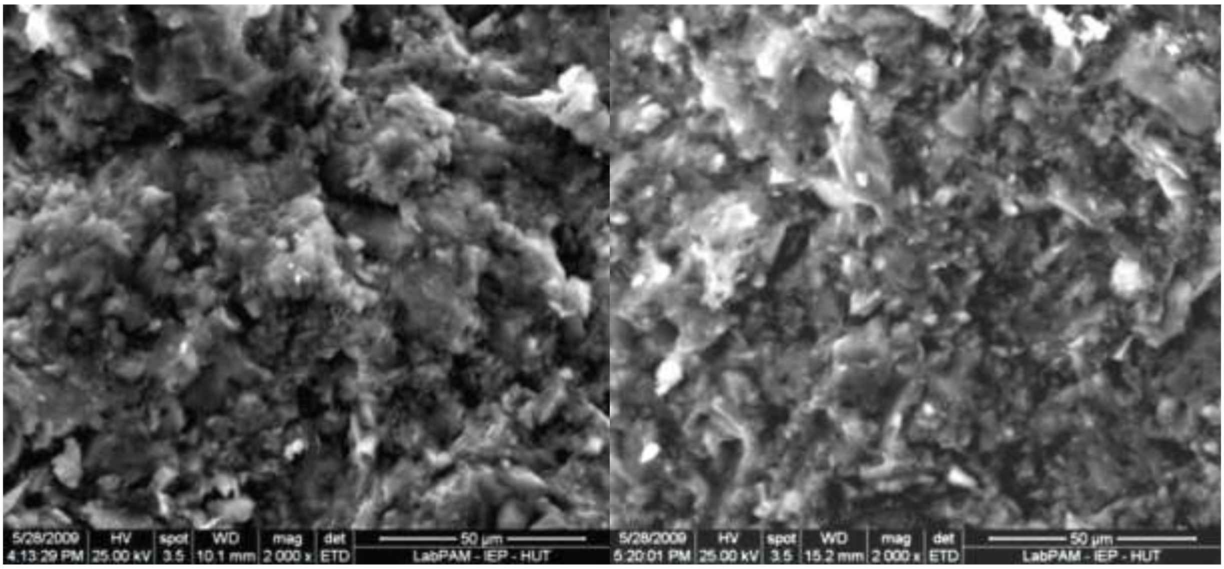


Figure 4. XRD of S15 at the age of 7 days

The content of Portlandite crystals $Ca(OH)_2$ are found in the pure cement sample is higher than S15 sample, it is a possibility that a part $Ca(OH)_2$ combined with $CaCO_3$ form hemicarboaluminate ($C_3A.0,5CaCO_3.0,5Ca(OH)_2.11,5H_2O$) [4,5,6]. It is consistent with previous studies and test results about strength.

3.2.3 SEM results

The results of SEM are shown in Fig. 5.



(a) S0 (b) S15

Figure 5. SEM pictures of the 7-age samples

After 7 days in hydration, the structure of S15 cement sample is closer and pore density is less than the structure of S0 cement sample. It would appear that limestone plays a role in initial nucleus actively and more evenly; moreover, it contributes to fill the pores.

4. CONCLUSION

Used up to 15% additives still maintains the basic properties of cement followed by Vietnamese standards.

Improved approximately 10÷20% strength at the early ages when we used to 15% additives.

The dehydration reduced. Specially, the bleeding rate reduced significantly from 16% in the pure cement sample to just under 3% when we used to 15% additives.

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