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Article

Effect of Curing Temperature and Free Lime Content in Fly Ash on Basic Properties and Autoclave Expansion of Fly Ash Mixtures

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Abstract. This study incorporates a detailed experimental program executed to determine the degree up to which the autoclave expansion of fly ash mixtures is sensitive to curing temperature. Three types of fly ashes were used and free lime was applied to increase the free lime contents in different fly ashes up to 10%. The influence of curing temperature on autoclave expansion of the mixtures was evaluated by curing under two temperatures, i.e., 23°C and 29°C for 24 hours after mixing. Experimental results exhibited that a higher free lime percentage resulted in a higher magnitude of autoclave expansion. It was observed that at a curing temperature of 23°C, the autoclave expansion was higher than the expansion of samples cured at a temperature of 29°C. Most of the mixtures, except the mixtures containing 40% fly ashes with the free lime amount of 10% and cured at a lower curing temperature, showed autoclave expansion values below the allowable limit recommended by ASTM C618.

Keywords: Fly ash, curing temperature, free lime, autoclave expansion.

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1. Introduction

Fly ash, a byproduct of coal combustion in thermal power plants is a waste material that is produced and disposed of in landfills in huge quantities. Various applications of fly ash were researched and introduced over time but still, the use of produced fly ash is limited to around 50% of worldwide production [1, 2]. The most widespread method to manage this huge amount of coal fly ash is to dispose of it or use it as landfill material. Fly ash is found to be beneficial for soil improvement, during the preparation of road bases, and as a raw ingredient for cement production. Furthermore, like several other industrial byproducts [3–8], fly ash also imparts valuable characteristics to cementitious materials. Numerous studies [9–19] indicate that fly ash can be used as a partial replacement for cement to improve compressive strength in the long term and concrete durability due to its pozzolanic reaction. The calcium hydroxide ($Ca(OH)_2$) formed during the hydration of Portland cement is consumed in the pozzolanic reaction with fly ash. Consequently, calcium-silicate hydrate (C-S-H) and calcium-aluminate hydrate are produced leading to the refinement of microporosity and hence improved compressive strength of cement fly ash mixtures is achieved. Moreover, the inclusion of fly ash resulted in reduced drying shrinkage and porosity of the concrete which ultimately led to lower chloride permeability and water sorptivity.

The mineralogy, characteristics, and various properties of fly ash differ considerably as the burning process used in electricity-generating power plants, source, type, and chemical compositions of fed coals are different in Thailand. Around 95% of fly ash is mainly produced by the Mae Moh power plant in Lampang province, Thailand. The Thai concrete industry has used fly ash to replace cement in concrete up to a certain limit in extensive amounts since 1997. Recently, fly ash from the Mae Moh power plant exhibited elevated free lime content [20, 21] which may cause an adverse effect on volume stability when added to concrete as a partial substitution of cement [22, 23]. Hence, it is essential to pay attention to the durability and other vital basic characteristics of concrete while using fly ash with a high percentage of free lime.

Volume stability is an important and desirable durability property of cement mixtures. The mortar or concrete with extensive volume instability is more probable to yield cracking and intolerable volume changes, which consequently results in damaging the structures. The expansion of concrete due to the usage of the unsound binder has been a serious cause of such deterioration. For years, the causes of unsoundness and expansion in cement and its mixtures containing fly ashes have been recognized and tested using various methods including accelerated soundness tests. In 1904, ASTM approved the pat test ASTM C189 as the accelerated method to check soundness and this test remained in use until 1940 when the autoclave test was first developed [24]. In the case of hydraulic cement, the hydration reactions of magnesium and calcium oxides cause possible delayed expansion, which can be determined by using the autoclave expansion test [25]. The performances of fly ash mixtures depend on several factors; for example, water-to-binder ratio, particle size distribution, chemical composition, and curing conditions as identified and characterized by many studies.

Curing temperature affects various concrete properties. Montri et al. [26] explored the influence of curing temperature and particle size on the mechanical properties of fly ash concrete and reported the strength development of fly-ash concrete using three curing temperatures (room temperature, 40°C and 60°C) and three plant-classified particle sizes. Three water-to-binder ratios were used i.e., 0.40, 0.45, and 0.50. The fly ash utilized by Montri et al. [26] was from the Mae Moh power plant. The test results showed that among the three cement replacement percentages used (20%, 30%, and 40%), 20% replacement resulted in the highest strength gain for all particle sizes and curing temperatures. Although the impact of raising the curing temperature from 40°C to 60°C was insignificant, the effect of curing at 40°C as compared to the room temperature was found relatively considerable. The rate of strength development increased as the curing temperature increased. This trend was very obvious at an early age of 7 days.

Hanehara et al. [27] observed the impact of mix proportion and curing temperature on the pozzolanic reaction of fly ash in cement paste by carefully investigating the production of $Ca(OH)_2$ and the pozzolanic reaction ratios. It was observed that in hardened paste, the pozzolanic reaction of fly ash cured at 20°C initiated at the age of 28 days while for the paste cured at 40°C, the reaction initiated even before the age of 7 days. Therefore, it was concluded that the curing temperature directly affects the reaction ratio which increases as the curing temperature increases.

ASTM C511 [28] specifies a curing temperature of 23±2°C in a moist cabinet or room and water storage tank for the testing of hydraulic cement and concrete. This temperature is also specified in ASTM C151 [25], which is the standard autoclave expansion test method of hydraulic cement. The 23±2°C curing temperature standard is widely used as the reference and applied in many Thai cement and concrete laboratories. However, it is expected that under higher curing temperature than 23°C (i.e. 29°C) paste mixtures tend to exhibit lower expansion. In tropical countries such as Thailand, where average annual temperature is much higher than 23°C (around 29-30°C in the case of central Thailand [29]), maintaining 23°C curing temperature is not close to real environment conditions. Recently, many standards have allowed 27±2°C as standard testing temperature for some laboratory tests as well as a range of 22°C to 32°C for some field tests in tropical regions [30]. Interestingly, even for autoclave test, some standards prescribe to maintain the temperature of the moulding room, dry materials, water and moist closet or moist room at 27±2°C [31]. As the difference of curing temperature can affect cement-fly ash mixtures reactions, it is vital to consider the influence of temperatures of different regions while formulating standards and specifications.

Therefore, this study is aimed at addressing the influence of free lime content and curing temperature on the fly ash concrete basic properties, emphasizing autoclave expansion, which was not included in our past research. In this study, along with the standard temperature of 23°C, another set of specimens was cured at a curing temperature of 29°C to evaluate the influence of curing temperature on the autoclave expansion. The basic properties of various cement-fly ash mixtures containing different free lime contents are also studied.

2. Experimental Program

2.1. Materials

Three natural fly ashes, designated as F(X), F(Y) and F(Z), from the Mae Moh power plant in Thailand and locally produced ordinary Portland cement (OPC) type I cement were used as the binders. The chemical and physical properties including the percentages of some of the main constituents of the cement and fly ashes along with the specific gravity and Blaine's fineness are shown in Table 1 and 2, which shows that each of the tested fly ash fineness is in a similar range. According to Thai industrial standards, TIS 2135 [32], F(X), F(Y) and F(Z) are categorized as Class 2b i.e., high CaO fly ashes. Moreover, the sulfur trioxide contents (SO_3) in F(Y) and F(Z) are greater than the allowable SO_3 content of 5% as identified by TIS 2135 [32].

In Thailand, the main source of fly ash production is the Mae Moh power plant and fly ash produced by this source has recently shown high content of free lime which may result in undesired expansion in concrete. Moreover, EN-450 limits the free lime content in fly ash not more than 2.5% [21]. As it is not possible to obtain fly ash samples that have different free lime contents while having the same other chemical compositions; therefore, free lime was added in the existing fly ashes to determine the behaviour of higher free lime fly ashes. The outcomes obtained from this investigation not only prove to be of immediate significance but also exhibit prospective value. This is particularly applicable in scenarios where higher free lime contents manifest in Mae Moh's fly ash in the future. To examine the influence of free lime content in fly ash on the fly ash concrete mixtures properties, the natural F(X), F(Y) and F(Z) fly ashes with free lime contents of 1.71%, 3.93%, and 3.06% were mixed with free lime from an outside source. In order to create three other high free lime fly ashes with 5%, 7%, and 10% free lime contents from each natural fly ash, external free lime was applied to all three natural fly ashes. In total, nine high free lime fly ashes with designations of F(X5), F(X7) and F(X10), F(Y5), F(Y7), F(Y10), F(Z5), F(Z7) and F(Z10) were prepared. The free lime content of the fly ashes was measured using a titration method adopted in a previous study [20]. River sand having a specific gravity of 2.60 conforming with ASTM C33 [33] was used as the fine aggregate.

The particle shape of Mae Moh fly ashes taken from SEM is presented in Fig. 1 which demonstrates spherical particles of the fly ash sample along with the irregular particles of free lime scattered around the fly ash particles. From EDX (Energy-dispersive X-ray) analysis, the irregular particles (#2) were confirmed to contain rich calcium content as demonstrated in Fig. 2, implying that they were free lime particles, while the spherical particle (#1) was rich in Si content, indicating that it was a fly ash particle.

Table 1. Chemical properties (from XRF analysis) of the materials used as binder.

Component (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Free lime
OPC Type I	18.93	5.51	3.31	65.53	1.24	2.88	0.75
Fly ash F(X)	35.71	20.44	15.54	16.52	2.00	4.26	1.71
Fly ash F(Y)	26.61	13.6	18.34	24.97	2.33	8.53	3.93
Fly ash F(Z)	25.22	13.88	17.39	26.25	2.38	9.44	3.06

Table 2. Physical properties of the materials used as binder.

Properties	OPC Type 1	F(X)	Fly ash F(Y)	F(Z)
Specific gravity	3.15	2.21	2.57	2.57
Blaine fineness (m^2/kg)	310	287	282	272

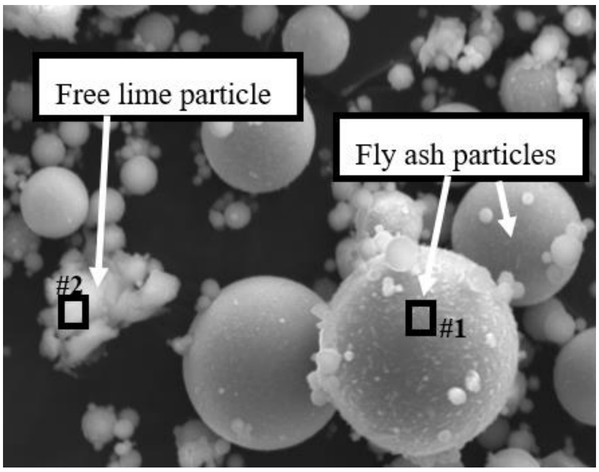
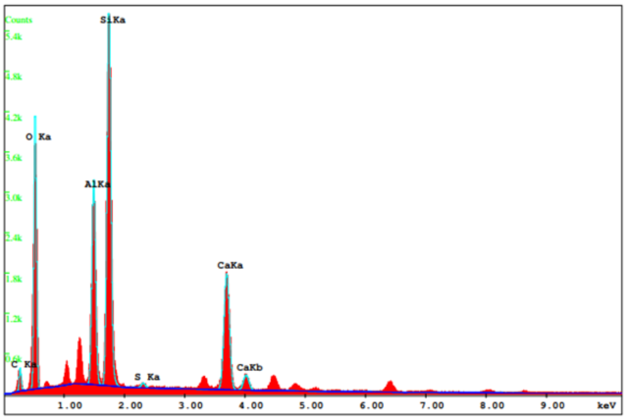
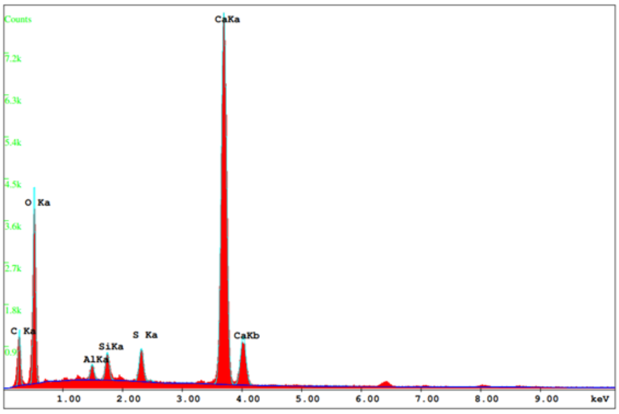


Fig. 1. SEM images of fly ash and free lime.



(a) Particle #1



(b) Particle #2

Fig. 2. EDX analysis results of (a) particle #1 and (b) particle #2.

2.2. Experiments and Sample Designations

The experimental program of this study is comprised of two phases. In the first phase, the influences of free lime content on the basic and durability properties of fly ash concrete mixtures were studied. The basic properties including setting time, water requirement and compressive strength were tested. A normal consistency test was conducted in accordance with ASTM C187 [34] to find out the required quantity of water to prepare hydraulic cement pastes for autoclave and setting time tests. In order to prepare the paste, 650 grams of binder is mixed with a measured quantity of water, as per ASTM C305 [35]. Setting times were found according to ASTM C191 [36] by means of the penetration of Vicat needle in the pastes of normal consistency. Compressive strength tests of hydraulic cement mortars were conducted as per ASTM C109 [37] using 50mm cube specimens. The mortar comprised of 1:2.75 parts by mass of cement and sand. The amount of water used for each test specimen, determined as per ASTM C311 [38], was sufficient to attain a flow of 110±5mm in 25 drops of the flow table. The water retainability of fly ashes was determined by following the methodology established in a prior research investigation [39]. Compressive strength tests of all mixtures were carried out using a Universal Testing Machine (UTM).

For the second phase, the influence of curing temperature on autoclave expansion was determined by exposing the test mixtures to two different temperatures during the curing phase i.e., 23°C and 29°C. Volume stability was measured by testing the autoclave expansion of paste specimens according to ASTM C151 [25]. To prepare test specimens for autoclave test, 25x25x285mm prisms having a 250mm gage length were prepared with pastes of normal consistency, as per ASTM C490 [40] and later on the test specimens were exposed to two different temperatures during the curing phases i.e., 23°C and 29°C. Curing temperature is defined as the ambient temperature of curing room in which test specimens were stored for 24 hours after mixing and before placing them in the autoclave chamber. After curing period, length of all samples was measured using a length comparator before placing in the autoclave chamber.

Test samples contained different fly ash types with 20%, and 40% of replacement of fly ash. At least three samples were prepared for each mixture to carry out autoclave expansion tests. Sand to binder ratio was controlled at 2.75 by weight for casting mortars. The designations for various mix proportions are given in Table 3 along with the ratio of cement and different fly ashes used for each mix.

3. Results and Discussions

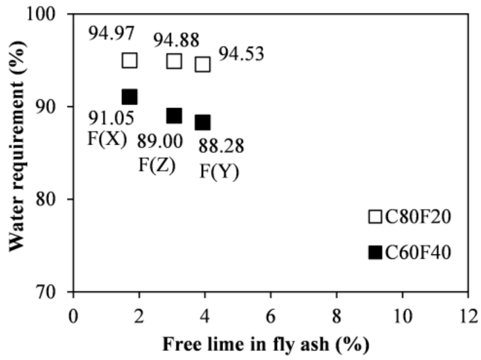
To better understand the behavior of various fly ash mixtures under different curing temperature, outcome of first phase is briefly discussed here before proceeding to the results of second phase.

3.1. Water Requirement

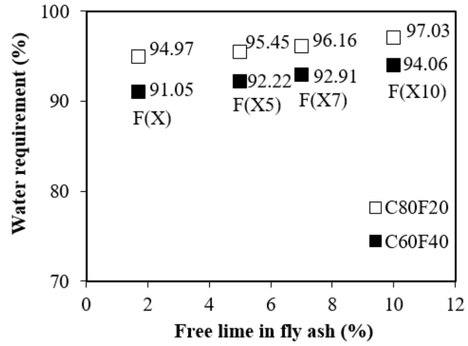
It was noticed that mixtures of all natural fly ashes needed lower water content than the cement-only mixture, to exhibit a similar degree of flow, as presented in Fig. 3(a). At 20% fly ash replacement, F(X), F(Y) and F(Z) mixtures had almost identical water requirement. As the amount of fly ashes increased from 20% to 40%, all fly ash mixtures had lower water requirement. At 40% fly ash replacement it was found that water requirement of mixture containing F(X) was slightly higher than those of mixtures containing F(Y) and F(Z), due to its higher water retainability [39] (see Fig. 4). It can be seen that F(X) has the highest water retainability of 18.54% whereas F(Y) and F(Z) have 14.27 and 14.97%, respectively. It implies that water is more absorbed and adsorbed by F(X) than F(Y) and F(Z). Therefore, the water requirement of mixtures containing 40% of F(X) to obtain the flow of 110% is higher than that of the mixtures containing 40% of F(Y) and F(Z). Figures 3(b) to 3(d) illustrate the correlation between the free lime contents and water requirements of F(X), F(Y) and F(Z) mixtures. It can be comprehended that an increase in the amount of free lime resulted in an increase of water requirement for different fly ashes to attain same degree of flow.

Table 3. Ratio of cement and fly ash as binder for different mixtures.

Mix designation	OPC Type I	Fly ash F(X)	F(Y)	F(Z)
C100	1	-	-	-
C80F(X)20	0.8	0.2	-	-
C60F(X)40	0.6	0.4	-	-
C80F(X5)20	0.8	0.2	-	-
C60F(X5)40	0.6	0.4	-	-
C80F(X7)20	0.8	0.2	-	-
C60F(X7)40	0.6	0.4	-	-
C80F(X10)20	0.8	0.2	-	-
C60F(X10)40	0.6	0.4	-	-
C80F(Y)20	0.8	-	0.2	-
C60F(Y)40	0.6	-	0.4	-
C80F(Y5)20	0.8	-	0.2	-
C60F(Y5)40	0.6	-	0.4	-
C80F(Y7)20	0.8	-	0.2	-
C60F(Y7)40	0.6	-	0.4	-
C80F(Y10)20	0.8	-	0.2	-
C60F(Y10)40	0.6	-	0.4	-
C80F(Z)20	0.8	-	-	0.2
C60F(Z)40	0.6	-	-	0.4
C80F(Z5)20	0.8	-	-	0.2
C60F(Z5)40	0.6	-	-	0.4
C80F(Z7)20	0.8	-	-	0.2
C60F(Z7)40	0.6	-	-	0.4
C80F(Z10)20	0.8	-	-	0.2
C60F(Z10)40	0.6	-	-	0.4



(a)



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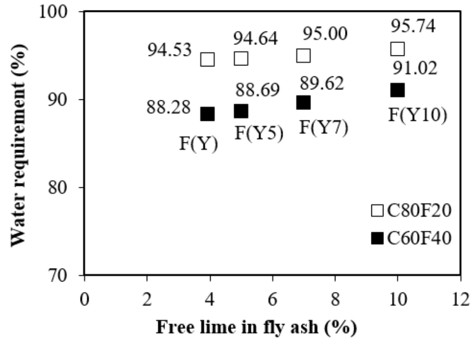
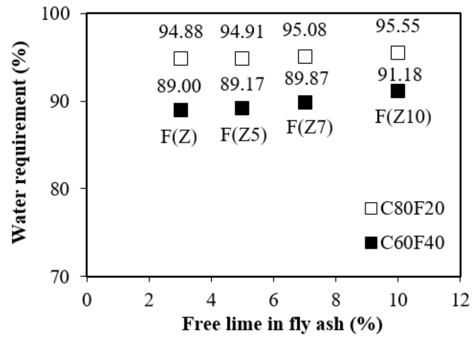


(c)



(d)

Fig. 3. Water requirement of fly ash mixtures containing different fly ash and free lime content.

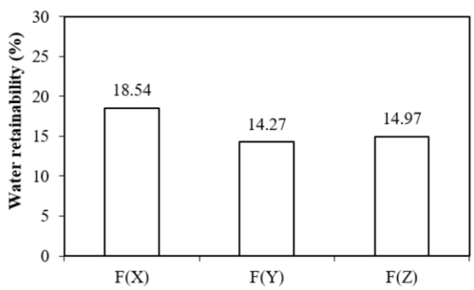


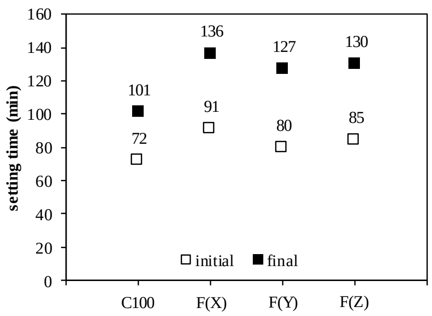
Fig. 4. Water retainability of basic fly ashes.

3.2. Setting Times

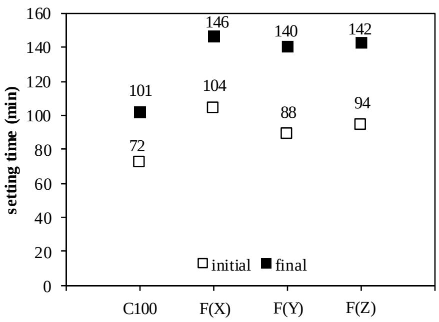
Figure 5 shows the outcome of initial and final setting time tests of the mixtures comprising of control mix and natural fly ashes F(X), F(Y) and F(Z). It can be seen from

Fig. 5(a) that when 20% of the cement is replaced with F(X), F(Y) or F(Z), both initial and final setting times of the mixtures are prolonged. Also, the mixtures containing F(Y) and F(Z), set faster than the mixtures containing F(X). In the case of F(Y) and F(Z) mixtures, higher CaO and SO_3 contents, as shown in Table 1, as well as lower water requirement than F(X), as discussed earlier, resulted in faster initial and final setting times, as compared to the mixtures containing F(X). Moreover, for mixtures with 40 % fly ash replacement, longer setting times were noticed (see Fig. 5(b)) as compared to mixtures containing 20% fly ash replacement, due to higher dilution effect and more delayed hydration reaction.

The influence of increasing the percentage of free lime on the setting times of F(X), F(Y) and F(Z) fly ash mixtures is displayed in Figs. 6, 7 and 8, respectively. The setting times of mixtures were shortened when their free lime contents were increased in both replacement percentages cases. This is because fly ash reacts with additional $Ca(OH)_2$ contributed by free lime, leading to quicker reaction and so shorter setting times.

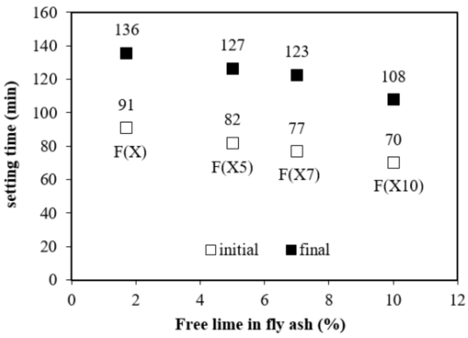


(a) 20% fly ash replacement

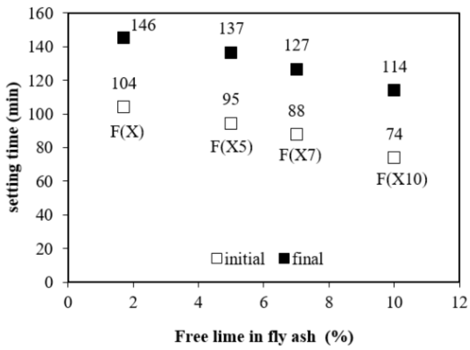


(b) 40% fly ash replacement

Fig. 5. Initial and final setting times of cement and natural fly ashes mixtures.

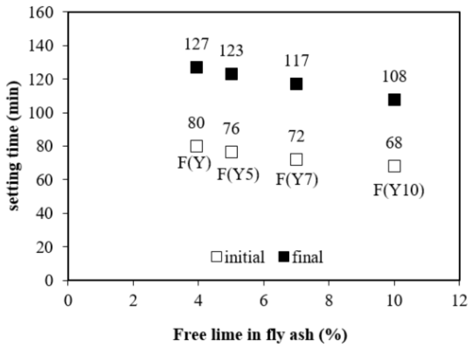


(a) 20%

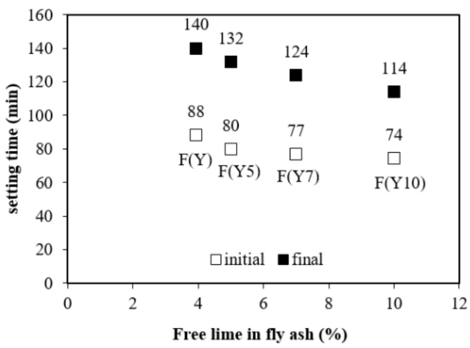


(b) 40%

Fig. 6. Setting times of 20% and 40% fly ash F(X) mixtures.

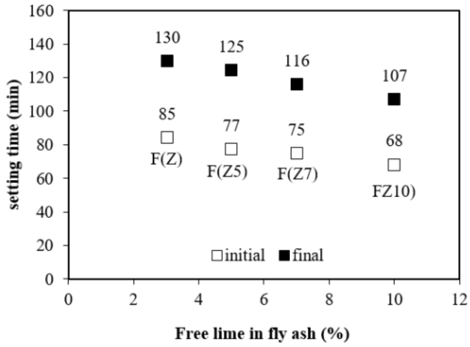


(a) 20%

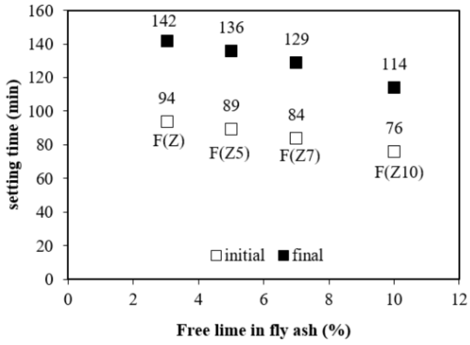


(b) 40%

Fig. 7. Setting times of 20% and 40% fly ash F(Y) mixtures.



(a) 20%

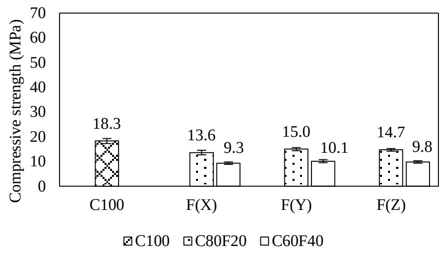


(b) 40%

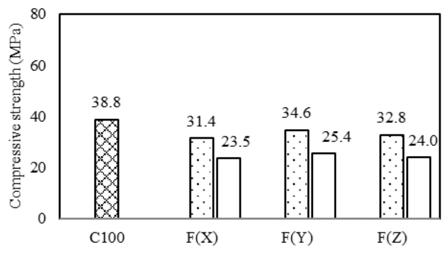
Fig. 8. Setting times of 20% and 40% fly ash F(Z) Mixtures.

3.3. Compressive Strength

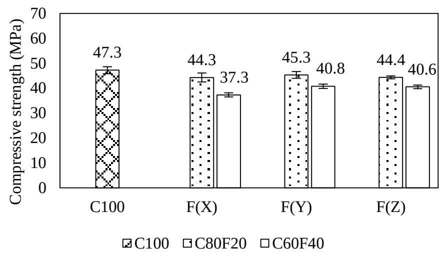
The 1-, 7-, 28- and 91-day compressive strength of cement-only mixture along with mixtures containing 20% and 40% natural fly ashes are shown in Fig. 9. It indicates that the 1-day compressive strength of F(Y) mixtures is slightly higher than that of F(X) and F(Z) fly ash mixtures. At 7 days, the compressive strength of F(Y) mixtures was clearly higher than that of the mixtures containing F(X) and F(Z), as presented in Fig. 9(b). The early-age compressive strengths of F(Y) mixtures are higher than F(X) and F(Z) mixtures because of higher percentage of free lime in F(Y) than F(X) and F(Z). It is observed in Fig. 9(c) and Fig. 9(d) that at the age of 28 and 91days, the compressive strengths of F(Y) mixtures were comparatively not much different from those of F(Z) and F(X) mixtures, particularly when 20% replacement was considered. This implies that the influence of free lime content of fly ash on long-term compressive strength is insignificant. However, the 91-day compressive strengths of mixtures containing 20% of F(X), F(Y) and F(Z), were higher than the compressive strength containing only cement, as displayed in Fig. 9(d). This is because of long-term pozzolanic reaction of the fly ashes.



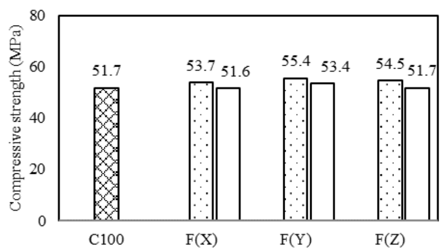
(a) 1 day



(b) 7 days



(c) 28 days



(d) 91 days

Fig. 9. Compressive strength up to 91 days of mixtures containing natural fly ash.

Figures 10 to 12 show the relative early-age and long-term compressive strengths of fly ash mixtures with high free lime contents as compared with the compressive strength of their respective natural fly ash mixtures. Figure 10 indicates that the mixtures containing F(X) with free lime content of 5%, 7% and 10%, show improvement in compressive strength, especially at the age of 1 day (around 10% to 20% improvement). This can be noticed for mixtures comprising of both 20% and 40% fly ash contents. The 91-day compressive strengths of F(X5), F(X7) and F(X10) mixtures were relatively equivalent to those of F(X) mixture.

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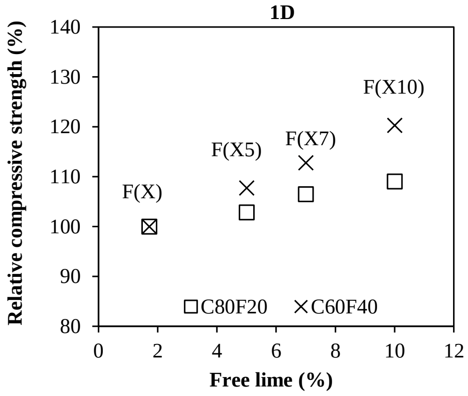
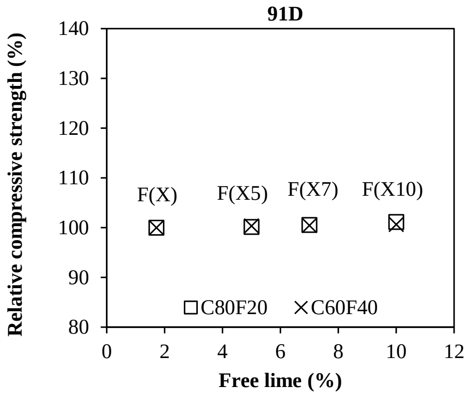
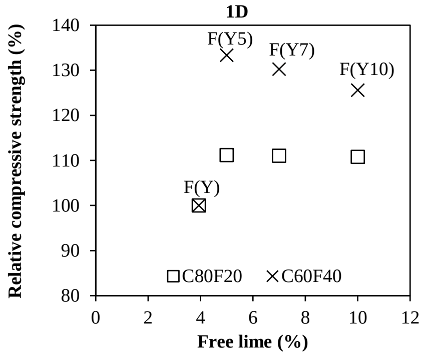


(a) 1 day

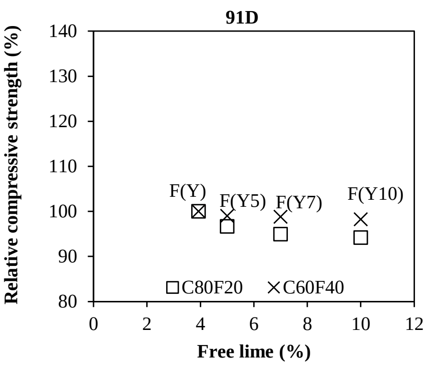


(b) 91 days

Fig. 10. Relative compressive strength of F(X5), F(X7) and F(X10) mixtures with respect to F(X) mixtures.

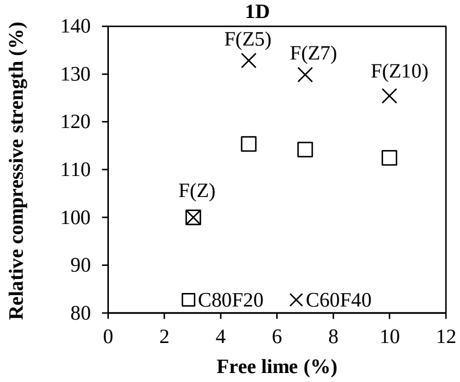


(a) 1 day

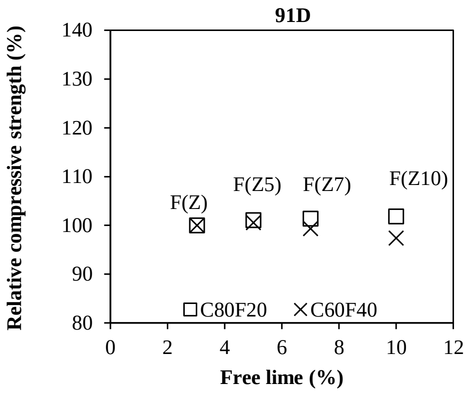


(b) 91 days

Fig. 11. Relative compressive strength of F(Y5), F(Y7) and F(Y10) mixtures with respect to F(Y) mixtures.



(a) 1 day



(b) 91 days

Fig. 12. Relative compressive strength of F(Z5), F(Z7) and F(Z10) mixtures with respect to F(Z) mixtures.

Figure 11 shows that mixtures containing F(Y) with a free lime content of 5%, 7% and 10%, resulted in an obvious increase in 1-day compressive strength beyond their control F(Y) mixture (up to 35% improvement). The 91-day compressive strengths of F(Y5), F(Y7) and F(Y10) mixtures were slightly lower than that of F(Y) mixtures. It can be observed from Fig. 12 that the mixtures comprising of F(Z) with increased amount of free lime, F(Z5), F(Z7), F(Z10), had enhanced 1-day strength (up to 30% improvement). The compressive strength of F(Z) at 91 days was not much influenced by the increased free lime content.

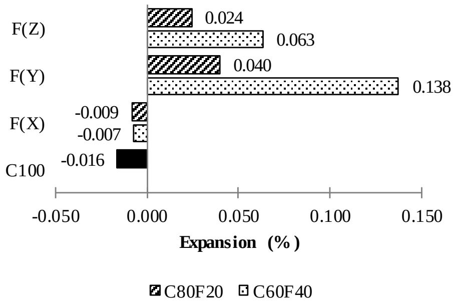
According to Fig. 10 to Fig. 12, the increase in the early-age compressive strengths of fly ash mixtures with the free lime inclusion is caused by the fly ash pozzolanic reaction with the supplementary $Ca(OH)_2$ produced from the reaction of water and the added free lime in the system. However, too high free lime content provides no further early-age strength improvement, as can be observed in Fig. 11(a) and Fig. 12(a) that the compressive strength of the F(Y) and F(Z) fly ash mixtures, consisting of 5% free lime is higher than that of mixtures containing fly ashes with 7% and 10% free lime contents. This attributed to the incompatibility of very high free lime amount in the mixtures with the low SiO_2 contents of F(Y) and F(Z). By comparing 1-day and 91-day compressive strengths, the improvement of compressive strength because of increased free lime is more noteworthy at an early age. The reduction of 91-day compressive strength of F(Y) mixtures as the free lime is increased to 5%, 7% and 10% can be observed in Fig. 11(b). However, their compressive strength was still higher than 92% of the respective original compressive strength of F(Y).

3.4. Autoclave Expansion

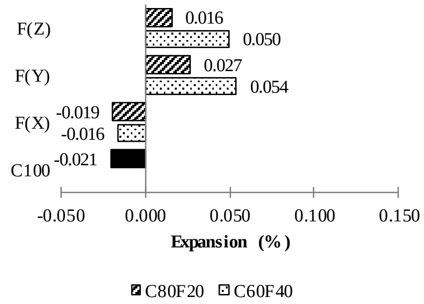
The concept of autoclave expansion is to check the volume instability caused by the hydration of free oxides, which are mainly free CaO and free MgO, to produce their respective hydroxide compounds [25]. Figures 13(a) and (b) demonstrate the results of autoclave expansion of the control mix along with the mixtures containing 20% and 40% of natural fly ashes, cured at 23±1°C and 29±1°C before the autoclave test. It can be observed that the cement-only mixtures as well as the F(X) mixtures showed shrinkage in comparison with the F(Y) and F(Z) mixtures. This is due to low free lime contents in F(X) and cement. Low free lime fly ash usually exhibits this shrinkage behavior [20]. Likewise, it can be noticed that autoclave expansion is higher when free lime content in fly ash is increased. As free lime content of F(Y) is the highest, it exhibited the highest expansion under both curing temperatures and fly ash replacement percentages cases. Higher replacement percentage also causes higher expansion.

The influence of both tested curing temperatures on autoclave expansion of different mixtures containing natural fly ashes, is also displayed in Figs. 13(a) and 13(b). It is shown that cement-only mixture and F(X) based mixtures showed shrinkage under 23°C and 29°C curing. Mixtures with F(Y) and F(Z) showed expansion in both 23°C and 29°C curing temperature cases. Mixtures comprising of 20% and 40% natural fly ashes and cured at 23°C showed higher expansion than the mixtures cured at 29°C. Even though the autoclave expansion of mixtures containing natural fly ashes was higher than that of mixtures containing only cement, particularly for the fly ashes containing higher CaO and free lime contents, the expansion results were still below the limitation of 0.8% in ASTM C618 [41].

Figures 14, 15 and 16 show the influence of total free lime content in the binders on the autoclave expansion under two curing temperatures. The binders in each figure contain F(X), F(Y) or F(Z) having free lime contents up to 10%. The reported total free lime content represents the total free lime content of the binder as determined by titration method [20] i.e., the total free lime content of the cement and fly ash mixtures not that fly ashes only.



(a) 23°C



(b) 29°C

Fig. 13. Autoclave expansion of fly ash mixtures exposed to curing temperatures of 23°C and 29°C.

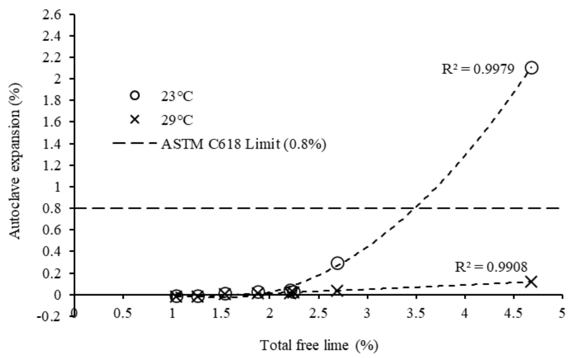


Fig. 14. Autoclave expansion of F(X), F(X5), F(X7) and F(X10) mixtures exposed to different temperatures.

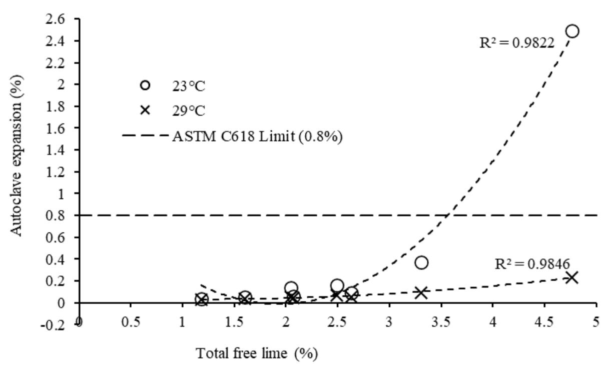


Fig. 15. Autoclave expansion of F(Y), F(Y5), F(Y7) and F(Y10) mixtures exposed to different temperatures.

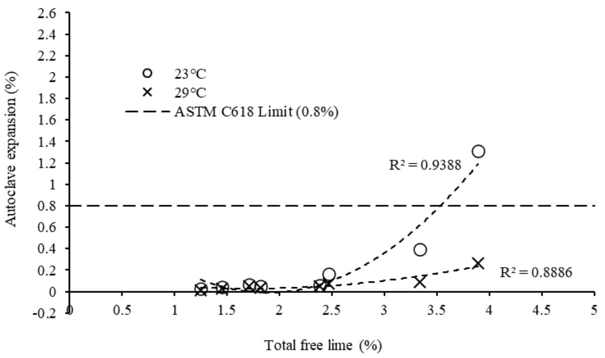


Fig. 16. Autoclave expansion of F(Z), F(Z5), F(Z7) and F(Z10) mixtures exposed to different temperatures.

Figure 14 illustrates that at 23°C, the magnitude of autoclave expansion increases as the total free lime content in the binder of F(X) mixtures increases. Higher total amount of free lime in the binders caused higher expansion. A total free lime content of 4.7% in the binder, in the case of C60F(X10)40 mixture, produced an expansion of 2.104%, which was much higher than 0.8% as limited by ASTM C618 [41]. At the curing temperature of 29°C, the similar trend of increased expansion with increasing total free lime content in the binder was also observed. However, the expansion values of the mixtures were smaller when compared with the values of the mixtures cured at 23±1°C at the same total free lime contents and were all below 0.8%.

Similar results were exhibited by the F(Y) and F(Z) fly ash mixtures as presented in Fig. 15 and Fig. 16, respectively. Mixtures prepared with these fly ashes showed increase in expansion with higher total free lime exposed in both curing temperatures. The expansion results of all mixtures exposed to both curing temperatures were still within the ASTM C618 limitation [41], except for the mixture with 40% F(Y10) (total free lime content of 4.8% in Fig. 15) and the mixture with 40% F(Z10) (total free lime content of 3.9% in Fig. 16) at the curing temperature of 23°C. The mixtures cured at 29°C showed lower expansion in comparison to the mixtures cured at 23°C, and their expansions were all lower than 0.8%.

The autoclave expansion occurs due to the development of $Ca(OH)_2$ and $Mg(OH)_2$ caused by the delayed hydration of free lime and MgO since the high steam pressure and high temperature in autoclave chamber quickens the hydration of both magnesia and lime [25]. However, other forms of CaO in the fly ashes are usually compounds which are not free, therefore different CaO contents in the tested fly ashes have an insignificant effect on the autoclave expansion when compared to the free lime. The SO_3 content also has little influence, since the reactions to produce primary ettringite have been completed before the samples get hardened while secondary ettringite is not stable under high temperature [42] in the autoclave. Therefore, the expansion due to free lime is dominant. Lower expansion in the case of higher curing temperature is seemingly according to the accelerated hydration reaction of free lime during the curing period prior to placing the mixtures in the autoclave chamber, whereas in the case of the mixtures exposed to a lower curing temperature, free lime experiences lower hydration degree during the curing phase. These explanations are supported by the fact that the hydration reaction of free CaO is exothermic reaction (Eq. (1)), and its hydration reaction rate follows the Arrhenius equation (Eq. (2)), as described by Shi et al. [43]. It supports that curing sample at 29°C causes higher hydration degree than curing sample at 23°C, providing that the generation of $Ca(OH)_2$ are accelerated during the curing period of the sample; therefore, delayed autoclave expansion is reduced. This agrees with the test results showing that expansion of sample cured at 29°C is decreased.

$$CaO+H_2O \rightarrow Ca(OH)_2 \tag{1}$$

$$K=Ae^{-Ea/RT} \tag{2}$$

where K is the reaction rate, A is the Arrhenius factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature.

From the test results, most of the fundamental and mechanical properties of high free lime fly ash mixtures have no adverse effect when compared with cement-only mixtures. However, high free lime fly ashes create more concern on volume instability or expansion. The autoclave expansion is selected to test expansion of high free lime fly ash mixtures due to its simplicity. As can be seen, higher free lime percentage in the mixtures causes higher expansion values. In most cases, the expansion values are lower than the recommended limit by ASTM C618 standard [41] except F(Y10) and F(Z10) mixtures cured at 23 °C. On the contrary, all high free lime fly ash mixtures exhibited expansions lower than 0.8% when cured at 29 °C. From this finding, it seems that the specified autoclave expansion limit of 0.8% is rather not appropriate for tropical countries. The limit of 0.8% may be too conservative for hot climate since the hydration of CaO and MgO can be accelerated before the setting resulting in lower expansion after hardening as compared with the case of low temperature climate. However, future intensive study is required for proper modification of the limit for an appropriate evaluation in hot climate.

4. Conclusions

The following conclusions can be drawn from this study:

1. The free lime inclusion in fly ash mixtures affects the fundamental properties of the mixtures, depending upon the amount of the added free lime. As increasing free lime content, the water requirement of mixtures increases. Moreover, the fly ash mixtures with higher free lime percentage cause accelerating setting times.

2. Higher free lime percentage in the tested fly ash contributes to improved early-age compressive strength.

However, free lime content has a negligible effect on the long-term compressive strength.

3. Variation of free lime content and curing temperature significantly influence the autoclave expansion. In general, the increase in free lime percentage in fly ash mixtures leads to an increased autoclave expansion. Higher curing temperature causes lower autoclave expansion.

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Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Somnuk Tangtermsirikul, photograph and biography not available at the time of publication.