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Effect and limitation of free lime content in cement-fly ash mixtures

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HIGHLIGHTS

- High free lime fly ash mixtures show satisfactory basic and mechanical properties.
- Higher free lime in fly ash leads to higher expansion in the durability tests.
- High free lime fly ash can partly replace cement if SO_3 content is low and vice versa.
- Tested fly ash with free lime content up to 4.23% can be utilized, if SO_3 <5%.
- If 5% > SO_3 < 10%, tested fly ash with free lime content up to 3.73% can be used.

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ABSTRACT

This study emphasizes the limitation of free lime content in fly ash. A detailed experimental program was carried out in order to evaluate the extent to which free lime content in fly ash can be tolerated, particularly for fly ashes with different sulfur trioxide contents. Some basic and durability properties of fly ash mixtures with varied free lime contents were considered. Four distinct types of fly ashes were obtained from two different sources, and free lime was added to obtain overall free lime contents of 5%, 7% and 10% for each type of fly ash. Water requirement, initial and final setting times, compressive strength, autoclave expansion, alkali aggregate reaction (AAR), and sulfate resistance tests of fly ash mixtures, containing various free lime contents, with two fly ash replacement percentages (20% and 40%), were conducted. Experimental results revealed that an increase in the free lime content caused an increase in water requirement. Higher free lime content also lead to faster setting times, improved compressive strength, and higher autoclave expansion. Mixtures with 20% fly ash replacement and free lime content up to 10% as well as mixtures with 40% fly ash replacement and free lime content up to 7.72% experienced autoclave expansion within the specified limit of ASTM C618. Similar trends of expansion were observed in cases of alkali-aggregate reaction and sulfate resistance tests where fly ash mixtures with high free lime led to higher expansion. In alkali-aggregate reaction testing, the mixtures with 20% fly ash replacement and free lime content up to 7.95%, as well as mixtures with 40% fly ash replacement and free lime content up to 10%, expanded less than the cement-only mixtures. The effect of added free lime was more severe in the sulfate resistance test, as fly ash mixtures tend to expand more than cement-only mixtures, especially in the case of fly ashes with very high SO_3 content (>5%). Test results also revealed that it is possible to utilize 20% of tested fly ash in a mixture as binder, with SO_3 content <5% and free lime content up to 10% while not compromising the basic and durability properties. In the case of 40% fly ash replacement, tested fly ashes with SO_3 < 5% and free lime content up to 4.23% can be utilized. In the case of high SO_3 content in fly ash, i.e., 8.53% and 9.44% in this study, the limit of free lime content of fly ash is reduced to 5.31% and 3.73%, for 20% and 40% fly ash replacements, respectively to satisfy the durability requirements.

1. Introduction

Fly ash, a by-product from the coal combustion process, is one of the most widely used supplementary materials in various

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high-performance cementitious systems. Various studies [1,2] have confirmed that depending upon the chemical composition and other factors, a partial replacement of ordinary Portland cement with fly ash results in an increase in long-term strength and durability of the resulting concrete. This strength increase is attributed to the pozzolanic reaction between fly ash and calcium hydroxide produced as a result of cement hydration. The pozzolanic reaction produces additional calcium silicate hydrate (C–S–H) product to fill up capillary pores, making the fly ash mixtures denser in microstructure as compared to normal concrete [3]. Chemical composition and mineralogy of fly ashes vary significantly depending on many factors including source, type and chemical composition of the coal, type of boilers, burning process, temperature, and emission control procedure, etc., of the power plants. Different countries' standards [4–6] cannot be applied directly because of the variations in properties and characteristics of fly ashes. In Thailand, although the production of fly ash started in early 1980's, the considerable use of fly ash as a cement replacement in concrete industry was initiated around mid-1990. In 2005, Thailand started using almost all of its fly ash in the concrete industry and is considered a successful country in terms of fly ash utilization [7]. In recent years, various studies have been conducted to modify and improve standards and guidelines for the use of fly ash in Thailand. Outcomes of these studies are reflected in Thai industrial standards, TIS 2135 [8].

The Mae Moh power plant of the Electricity Generating Authority of Thailand (EGAT) is one of the main production sources of fly ash, contributing around 90% of total national production. Recently, fly ash obtained from this source has shown increased content of free lime [9]. During the coal burning process, when heated, calcium carbonate ($CaCO_3$) decomposes into calcium oxide (CaO) and carbon dioxide (CO_2). It is a reversible process and a re-carbonation reaction can take place due to the reaction of CaO and CO_2 forming $CaCO_3$. The degree of re-carbonation reaction depends mainly on the porosity and reactivity of the resulting CaO with CO_2 and sintering at high temperatures [10]. The thermal disruption of $CaCO_3$ results in unreacted CaO which explains the occurrence of free lime in fly ash. Free lime may result in undesired expansion and volume instability when used in concrete as a cement replacement. Therefore, due consideration must be paid toward durability issues and time-dependent properties of concrete containing fly ash with elevated percentages of free lime.

In ASTM C618 [4] and many other standards, no limit is established for free lime content of fly ash. However, EN-450 [6] restricts the free lime content to 1%, or up to 2.5% if the autoclave expansion is still within the established limits. Kaewmanee et al. [9] conducted a comprehensive study on expansion properties of fly ash mixes, with various free lime contents and reported a set of experimental results to clarify the effect of free lime content on fly ash mixes. Results showed that basic properties (normal consistency and water demand) were not much affected by free lime added, and a free lime content up to 4.51% had only slight effect on chemical properties of fly ash–cement mixtures. The values of autoclave expansion of the tested mixtures, with 4.51% free lime content in fly ash, were observed to still remain within the limit imposed by ASTM C618. It was further concluded that mixtures with fly ash acquiring 4.51% free lime contents led to higher expansion due to alkali-aggregate reaction (AAR), but the expansion was still smaller as compared to the expansion of cement-only mixture.

Free lime content in fly ash is not the only cause of volumetric expansion in concrete. In recent times, fly ash obtained from the Mae Moh power plant has not only shown increased contents of free lime, but also tendency of higher sulfur trioxide (SO_3) content, which may contribute to long term expansion and volume instability. ASTM C618 limits the sulfur trioxide (SO_3) content to 5%. Although Kaewmanee et al. [9] concluded that free lime content up to 4.51% can be used, still there is research gap for of further investigation to simultaneously consider the effect of high free lime and high SO_3 content in fly ashes as well as their limits of free lime and SO_3 contents. This study is an attempt to further explore the limitation and knowledge of the effect of high free lime content in different fly ashes of Thailand, particularly in the case of fly ashes with different sulfur trioxide (SO_3) contents.

2. Experimental program

2.1. Materials

Four primary fly ashes F(A), F(B), F(C), and F(R) from two different sources and an ordinary Portland cement (OPC) type I, were used in this study. F(A), F(B), and F(C) were obtained from the Mae Moh power generating plant of the Electricity Generating Authority of Thailand (EGAT) in Lampang province (located in the north of Thailand), whereas F(R) was obtained from the coal burning thermal power plant in Rayong province (Eastern part of Thailand). Table 1 illustrates the physical properties of the mentioned materials. Chemical compositions of the materials, as listed in Table 2, are determined by XRF which is mainly used to measure total elemental composition only [11] whereas, free lime content is measured using titration method [9].

Based on chemical requirements of TIS 2135, F(R) was categorized as Class 2a (low CaO fly ash) whereas F(A), F(B) and F(C) were classified as Class 2b (high CaO fly ash). The amount of sulfur trioxide (SO_3) in F(B) and F(C) exceeded the maximum allowable limit of 5%, as specified by TIS 2135.

Free lime from an external source was added in F(A), which had a natural free lime content of 1.71%, to prepare three additional high free lime fly ashes. These fly ashes were designated as F(A5), F(A7) and F(A10) with the total free lime contents of 5%, 7% and 10%, respectively. Similarly, F(B5), F(B7), F(B10) were prepared by adding free lime in F(B) (with a natural free lime content of 3.93%), and F(C5), F(C7), F(C10) were prepared by adding free lime in F(C) (with a natural free lime content of 3.03%), in order to obtain the total free lime contents of 5%, 7% and 10%, respectively. As mentioned earlier, Mae Moh power generating plant contributes almost 90% of the total fly ash national production whereas other sources, including the source of F(R), produce a small amount of fly ash. Also, free lime content of F(R) (0.03%) is considerably lower than that of Mae Moh fly ashes (1.71–3.93%) used in this study, therefore free lime was added only to the Mae Moh fly ashes in order to determine the effect of high free lime content on the properties of cement-fly ash mixtures. Table 3 shows the physical characteristics of the fly ashes after the addition of free lime in the primary fly ashes.

In this study, river sand compatible with ASTM C33-92a [12], with a specific gravity of 2.60 was used as the fine aggregate.

Table 1
Physical properties of ordinary Portland cement type I, Mae Moh fly ashes A, B, C, Rayong fly ash R and free lime.

Physical properties	OPC type I	Fly ash A	Fly ash B	Fly ash C	Fly ash R	Free lime
Specific gravity	3.15	2.21	2.57	2.57	2.17	2.96
Blaine fineness (cm^2/g)	3100	2867	2820	2722	2723	3749

Table 2
Chemical compositions of ordinary Portland cement type I, Mae Moh fly ashes A, B, C and Rayong fly ash R.

Chemical compositions (mass %)	OPC type I	Fly ash A	Fly ash B	Fly ash C	Fly ash R
SiO_2	18.93	35.71	26.61	25.22	61.46
Al_2O_3	5.51	20.44	13.6	13.88	20.27
Fe_2O_3	3.31	15.54	18.34	17.39	5.56
CaO*	65.53	16.52	24.97	26.25	1.73
MgO	1.24	2	2.33	2.38	0.96
Na_2O	0.15	1.15	1.75	1.4	0.73
K_2O	0.31	2.41	1.77	1.92	1.36
SO_3	2.88	4.26	8.53	9.44	0.38
LOI	–	0.49	0.53	0.56	5.38
Minor oxides	2.14	1.48	1.57	1.56	2.17
Total	100	100	100	100	100
Free lime*	0.75	1.71	3.93	3.06	0.03
Equivalent sodium oxide ($Na_2O + 0.658\ K_2O$)	0.35	2.74	2.91	2.66	1.62

* CaO content includes the free lime content.