

EFFECTS OF COMBINATIONS OF LIMESTONE POWDER AND METAKAOLIN ON MORTAR COMPRESSIVE STRENGTH DEVELOPMENT

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Abstract

Cement production is a major contributor to carbon dioxide (CO₂) emissions, and concrete is one of the most widely used building materials in the world. To reduce CO₂ emissions from cement, supplementary cementing materials have been widely introduced in mortar and concrete mixtures. This research will explore the mechanism that determines the development of compressive strength in mortar made with partly substituted cement and a mixture of limestone powder and laboratory-quenching heat-treated kaolinite clay (also called metakaolin). Metakaolin is rich in Southeast Asian countries and needs further investigation to adopt in cement systems. Limestone powder and metakaolin constitute 45% of the binding cement ingredient by weight (dry). The strength was evaluated using mortar, and the microstructure was determined using paste. The results show that at 28 days, the compressive strength of mortar containing 45% cement substitution by 15% limestone powder and 30% metakaolin with 1% PCE (per B45S 1:2) was 97% relative to the reference mortar. However, due to the impurities in metakaolin, its synergistic interaction is limited, which results in the compressive strength being lower than anticipated.

Keywords: Compressive strength; limestone powder; metakaolin; ternary blend mortar

Introduction

Currently, the consumption rate of Portland cement worldwide is rapidly increasing, which has resulted in a steady increase in global cement production. Annual production remained around 1 billion tons until the 1990s (Uwasu *et al.*, 2014), but then grew quickly to reach nearly 4.1 billion tons in 2020, primarily in developing nations. Unfortunately,

this growth has hurt the environment, with increased carbon dioxide (CO₂) emissions. To address this issue, numerous studies have been conducted to explore substitute materials for cement to decrease the clinker factor and greenhouse effect. One such material is supplementary cementitious materials (SCMs), also known as pozzolan, which is used in

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conjunction with Portland cement and contributes to the properties of hardened concrete through hydraulic or pozzolanic activity, or both (Prasittisopin and Trejo, 2013; Thomas, 2013; Prasittisopin and Sereewatthanawut, 2019; Sereewatthanawut *et al.*, 2021).

Limestone is a type of rock formed from the sedimentation of calcium carbonate (CaCO_3) which is classified as carbonate rock. It is commonly used as a partial replacement for cement and is allowed in amounts up to 15% according to ASTM E595 (ASTM E595-15, 2015). The benefits of adding limestone powder to concrete include faster hydration, a slight increase in the early strength, improved control over bleeding, and a reduction in initial and final setting times. These rocks contain over 50% carbonate minerals, with calcite (pure CaCO_3) or dolomite (calcium-magnesium carbonate, $\text{CaMg}(\text{CO}_3)_2$) being the most common. Limestone powder is created by grinding limestone rock into very small particles. As a binding material, fine limestone can fill the pores of the concrete, resulting in a filler effect. Additionally, the fine limestone powder may accelerate the early hydration of cement clinkers. However, there are limitations to using limestone powder in place of cement due to the dilution effect and free lime effect (Van Leeuwen *et al.*, 2016; Panesar and Zhang, 2020; Win *et al.*, 2022; Sereewatthanawut *et al.*, 2023).

Metakaolin is a SCM that is of great interest as a substitute for cement. It is a dehydrated material derived from kaolinite clay, which can be readily found in both natural and industrial settings. Although kaolinite clay is typically white, it can be discolored by impurities, resulting in hues such as red or light brown. Metakaolin is produced at a relatively low temperature (600-800°C), which is considerably lower than the temperature required to produce clinker (1,450°C). Moreover, metakaolin reduces CO_2 emissions by roughly 96 kg per ton (Perlot *et al.*, 2013), making it an eco-friendly concrete material. Its use in concrete can substantially reduce the permeability of the material by decreasing the size of pores and transforming many finer particles into discontinuous pores. Metakaolin also enhances the compressive and flexural strengths of concrete and reduces the heat of hydration, resulting in better shrinkage and crack control (Brooks and Johari, 2001). However, the metakaolin is impure because the limited source of pure kaolinite clay in Thailand.

Kaolinite can be created through residual weathering, hydrothermal alteration, or as a sedimentary mineral. Metakaolin, an artificial pozzolanic material, is produced by dehydrating the clay mineral kaolinite, with a theoretical formula of $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or AS_2 . Thermal activation at 600-

900°C increases disorder in the alumina sheet and causes particle breakdown of the crystal lattice structure into an amorphous form (San Nicolas, 2012). The dehydroxylation process of kaolinite is affected by various parameters, including temperature, heating time, and cooling parameters (Ilić *et al.*, 2010). When used as a cement replacement material, silica, and alumina from the pozzolanic material react with calcium hydroxide (CH), which is the product of Portland cement hydration, resulting in the production of secondary cementitious products (C-S-H or C-A-H). This increases the number of cementitious products and enhances strength.

Considering the numerous beneficial aspects of limestone powder and metakaolin, it would be a novel notion to investigate the impact of using these materials, which are abundantly found in Thailand and Southeast Asian countries, as partial replacements for cement in mortar while also exploring the mechanisms and reactions that influence compressive strength. This research will consider the quality and quantity of limestone powder and metakaolin and how they affect compressive strengths such that these low greenhouse gas systems can be sustainably adopted in cement and concrete industries.

Materials and Methods

Materials

The materials used in this study included Portland cement type I (Elephant brand) that meets the ASTM C150 standard (ASTM C150/C150M-22, 2022), limestone powder obtained through the grinding of rocks from Saraburi Province, metakaolin obtained from the heat treatment of kaolinite clay from Uttaradit Province, standard sand that meets the ASTM C33 standard (ASTM C33-18, 2018), clean water with a pH value of 7.0, and the Glenium ACE32 high-range water-reducing superplasticizer. The sand used had a percentage absorption of 0.63 and a specific gravity of 2.61 (ASTM C128-15, 2015).

Mixing Proportions, Mixing, and Curing

The mortar specimens were mixed according to the proportions shown in Table 1, with a fixed water-to-cement ratio or water-to-binder ratio of 0.485 and a cement-to-sand ratio or binder-to-sand ratio of 1:2.75 (ASTM C109/C109M-16, 2016). The ratio of limestone powder to metakaolin used was 1:1, 1:2, and 2:1, and 100% Portland cement mortar was used as a reference. Two mortar systems were used: one with a superplasticizer and one without, with the admixture dosage determined by the flow

table test (ASTM C1437-20, 2020). The paste samples were proportioned in the same manner as the mortar, but without sand. The mortar specimens were cubes with dimensions of 50×50×50 mm and were mixed using a mixer and following the mixing procedure outlined in ASTM C305 (ASTM C305-20, 2020), which is the standard practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency.

Heat of Hydration Reaction Determination

To determine the heat generated from the hydration reaction of cement paste and cement-limestone powder-metakaolin paste, an isothermal calorimeter was used following the ASTM C186 standard (ASTM C186-17, 2017).

Compressive Strength Test

In accordance with ASTM C109 (ASTM C109/C109M-16, 2016), the compressive strength test was conducted on hydraulic cement mortar specimens using three cube samples per set. The compression test was performed after 1, 3, 7, and 28 days of curing time.

Results and Discussions

Heat Treatment of Kaolinite Clay

Finding pure kaolinite clay in Thailand is challenging, as the available clay in the market contains a low percentage of kaolinite and is usually mixed with other reactive and non-reactive clays and substances. To obtain a higher concentration of kaolinite, researchers collected samples from Uttaradit province, where the clay had a kaolinite content of about 20%. The researchers then subjected the kaolinite clay to laboratory thermal treatment to obtain metakaolin, which is a metaphase of kaolinite. The burning temperature was determined by analyzing the dehydroxylation process using Thermogravimetry (TG), as shown in Figure 1.

The results revealed that temperatures below 450°C caused the release of water from the clay's surface and pores, indicating a pre-dehydration process.

Table 1. Mixture proportion for powder binders

	Cement (%)	Limestone (%)	Metakaolin (%)
100% CM	100	0	0
B45 1:2 *	55	15	30
B45 1:1 *	55	22.5	22.5
B45 2:1 *	55	30	15
B45S 1:2 *	55	15	30
B45S 1:1 *	55	22.5	22.5
B45S 2:1 *	55	30	15

* The ternary blends are labelled as "BxxS y:z", xx is the level of cement substitution, S is superplasticizer is added and no alphabet mean without admixture, y is the proportion of limestone powder by dry weight of cement and z is the proportion of metakaolin by dry weight of cement.

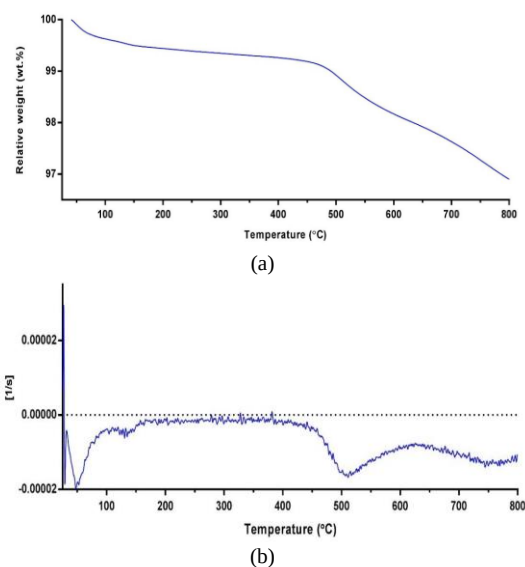


Figure 1. TG analysis curve (a) mass loss of kaolinite clay (b) Time derivative of mass loss of kaolinite clay

Table 2. The chemical and physical properties of the main constitutions

Oxide/Compound	Cement (wt%)	Limestone (wt%)	Metakaolin (wt%)
CaO	69.20	-	-
CaCO ₃	-	97.95	-
SiO ₂	18.05	1.65	76.98
Al ₂ O ₃	3.93	-	14.03
K ₂ O	0.56	-	4.70
TiO ₂	0.36	-	0.16
MgO	-	-	1.99
SO ₃	4.07	-	-
Fe ₂ O ₃	3.83	0.40	2.14
Total	100.00	100.00	100.00
Blain surface area (m ² /g)	0.117	2.240	1.180
Specific gravity	3.116	2.674	2.420

Between 450°C and 800°C, metakaolin was formed. Thus, the researchers selected a burning temperature of 800°C and a duration of 1.5 h for the thermal treatment. After heating, the kaolinite clay was quickly quenched to room temperature to prevent amorphous recrystallization.

Properties of Raw Materials

Chemical and Physical Properties of Powder

Table 2 provides the chemical composition, quantifications determined by the X-ray fluorescence method, and some physical properties of the three primary raw materials. The key components of cement are calcium oxide, silica oxide, and alumina oxide. Limestone powder is composed of approximately 98% CaCO_3 , while metakaolin is a pozzolanic material that contains silica oxide and alumina oxide as its primary components.

Workability of Blend Mortar Tested by Flow Table Method

To adjust the workability of the ternary blend mortar, the researchers added polycarboxylic ether superplasticizer (PCE), specifically Glenium ACE32, and determined the appropriate dosage by adjusting the amount of superplasticizer used. The aim was to achieve a percentage of flow table for the ternary blend mortar that was nearly identical to the reference cement mortar, while also ensuring that the percentage of flowability remained within the standard normal consistency range of $110 \pm 5\%$. The results of each mixed proportion can be found in Table 3. In this study, the researchers used 1% of PCE based on the dry weight of the binder.

Heat of Hydration

Effect of Ternary Blend on Heat of Hydration

Figure 2 displays the heat flow recorded based on the quantity of binder, while Figure 3 exhibits the cumulative heat. The results indicate that substituting some cement with metakaolin and partially with limestone powder reduces the heat generated during the hydration process compared to using 100% cement paste.

Mechanical Strength

Figure 4 presents the compressive strength test results for all mortar specimens at 1, 3, 7, and 28 days

days. For all mixed proportions, the compressive strength values were lower than the reference at all ages. Among the ternary blend mortar specimens, the best result was achieved with B45S 1:2 mortar, which had a 45% blend of cement replaced by limestone powder (15%) and metakaolin (30%), along with 1% PCE. This mixture reached a compressive strength almost as high as the control

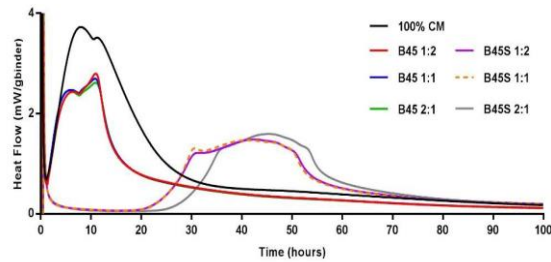


Figure 2. Heat flow reported on basis of grams of binder by isothermal calorimeter of the blend paste compared to reference cement paste (100% CM) until 100 h

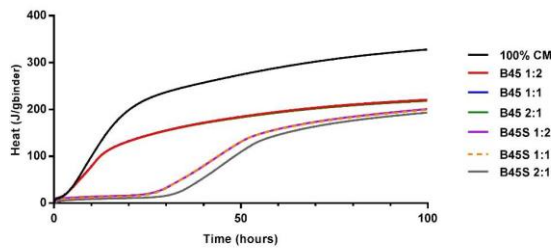


Figure 3. Cumulative heat of binder paste compared to reference cement paste (100% CM) until 100 h

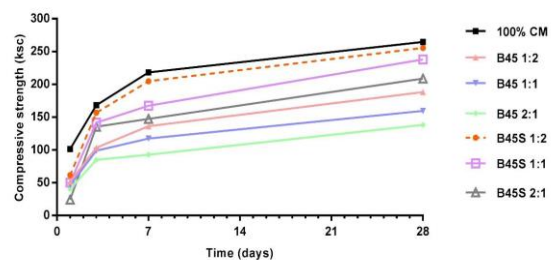


Figure 4. Compressive strength of blended mortars at 1, 3, 7 and 28 days

Table 3. The percentage of flowability for fresh mortars with various PCE dosages

Formula	Amount of PCE (wt% of binder)		
	0	1	2
	Flow value of mortar (%)		
100% CM	110.99	-	-
B45S 1:2	103.35	110.24	140.57
B45S 1:1	105.31	113.19	140.75
B45S 2:1	108.26	112.21	141.73

reference, with a relative strength of approximately 97% at 28 days.

Conclusions

This study aims to analyze the compressive strength development of mortar with 45% replacement of cement by combining limestone powder and heated-treated kaolinite clay with different ratios of 1:2, 1:1, and 2:1, with and without PCE superplasticizer, in comparison to the 100% cement mortar reference. The research indicates that the mortar with 45% cement replacement by 15% limestone powder and 30% metakaolin with 1% PCE achieved the highest compressive strength value, which was almost the same as that of the 100% reference cement mortar. The primary mechanism affecting compressive strength is outlined as follows:

- The PCE facilitates the dispersing mechanism in the early stage of the reaction. The main polymer chains (carboxylate group-COO⁻) adsorb on the surface of cement particles, giving them a negative charge that leads to electrostatic repulsion between the cement particles. This causes cement particle rearrangement and improves the compactness of the hardened mortar, resulting in a decrease in total porosity. This is why the superplasticizer system produces higher compressive strength compared to the non-superplasticizer system.
- The quality of metakaolin affects the development of compressive strength in ternary blend mortar. The presence of impurities in metakaolin limits the reaction and reduces the level of aluminate oxide in clay, leading to lower-than-expected compressive strength.

On-going research has been conducted for other mechanical properties and long-term performance. It should be noted that the life-cycle cost and life cycle assessment of these systems should be performed to quantify their benefits.

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