- Technical Paper -

EFFECTS OF CALCINED CLAY AND LIMESTONE POWDER AS SUPPLEMENTARY CEMENTITIOUS MATERIALS ON SHRINKAGE

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ABSTRACT

This study investigates autogenous and drying shrinkage of paste samples incorporating calcined clay (CC) and limestone powder (LP) as supplementary cementitious materials. The tested mixtures included binary and ternary blends with 30% replacement by CC and LP, alongside a cement mixture without CC as a control. The results indicate that mixtures containing CC exhibited greater autogenous shrinkage compared to the control, the shrinkage was increased by the addition of LP. Conversely, CC reduced drying shrinkage, resulting in lower values than those observed in the control mixture.

Keywords: calcined clay, limestone powder, shrinkage, supplementary cementitious materials, weight change

1. INTRODUCTION

Concrete is the second most consumed material on earth, with cement constituting its primary component in construction. Due to the production process of cement clinkers, CO_2 emission is unavoidable. The use of supplementary cementitious materials (SCMs) such as fly ash and ground granulated blast furnace slag to replace cement is one of the popular solutions to reduce CO_2 emissions. In Thailand, fly ash has traditionally been employed as the predominant SCM to partially replace cement. Recently, however, the availability of fly ash has diminished due to limited operational coal-fired power plants, leading to supply shortages.

Limestone calcined clay cement (LC^3) is a ternary blended cement [1] consisting of approximately 50% clinker, 25-30% calcined clay, 15% limestone powder, and optionally 5% gypsum. Calcined clay contributes alumina, while limestone powder provides calcium carbonate, enabling the formation of calcium carboaluminate. This combination creates a synergistic effect, improving concrete durability, density, and mechanical properties. Clay deposits are typically found in regions near the equator [2], with kaolinite content varying by location [1]. In Thailand, kaolinite content of raw clay ranges between 30-40% [3]. To develop pozzolanic properties, the raw clay is heated to between 600 to 900 °C, leading to the breakdown of its crystal structure [2], [4]. Limestone powder, on the other hand, can be sourced from stone waste or dust, making it a sustainable alternative.

Numerous investigations have examined the mechanical and durability characteristics of LC^3, including compressive strength and shrinkage behavior [2] - [3], [5] - [7]. Notably, some studies have reported substantial autogenous shrinkage when LC^3 is employed [6] - [7]. Although the kaolinite content of calcined clay in LC^3 research has ranged from 17% to 95% [6] – [12], most prior work has focused on clay with higher kaolinite levels. Consequently, there have been limited examinations of calcined clay with comparatively lower kaolinite content as an SCM. For instance, Sudsawong observed that calcined clay derived from raw clay containing approximately 40% kaolinite exhibited reduced workability and showed higher autogenous and total shrinkage compared to cement mixture [13]. Despite these findings, the mechanisms of calcined clay with low kaolinite in cementitious systems remain insufficiently understood.

Accordingly, this study aims to elucidate the effects of calcined clay originating from Thailand, with a kaolinite content of 25% (lower quality clay than usual), on autogenous and drying shrinkage in cement-based materials. The shrinkage behavior of paste mixes incorporating calcined clay and limestone powder is compared to that of a reference cement paste without the clay.

2. EXPERIMENTAL PROGRAMS

2.1 Materials

The materials used in this study were classified into two groups: cement and supplementary cementitious materials. One type of Portland composite cement (PCC), a hydraulic cement containing approximately 10% limestone powder as a clinker replacement in accordance with the Thai standard (TIS 2594), was used. In Thailand, the use of Portland cement Type I was discontinued in 2024, while hydraulic cement for general use (type GU) containing up to 10%

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limestone powder has been increasingly used since 2020 and is now the primary cement type. Two types of SCMs were utilized, which were calcined clay (hereafter, CC) and limestone powder (hereafter, LP). All three materials were obtained from Siam Cement Group Co., Ltd. in Thailand. The chemical compositions of the binders, determined by XRF analysis by the company, are presented in Table 1. Mineral compositions of the tested SCMs and cement from Rietveld analysis are shown in Tables 2 and 3, respectively. Physical properties of the binders are listed in Table 4.

Table 1 Chemical compositions of tested binders

Chemical compositions (% by weight)	PCC	CC	LP
SiO_2	18.31	60.53	0.69
Al_2O_3	5.04	25.57	0.32
Fe_2O_3	2.97	7.06	0.19
CaO	63.83	0.45	54.10
MgO	1.04	0.55	0.79
SO_3	2.86	0.24	-
Na_2O	0.25	0.26	0.02
K_2O	0.27	1.12	0.01
TiO_2	0.25	1.44	0.02
P_2O_5	0.06	0.07	0.03
MnO	0.07	0.05	0.01
LOI	4.87	2.62	43.82

Table 2 Mineral compositions of tested SCMs

Mineral compositions (% by weight)	CC	LP
Calcite	0.06	98.56
Quartz	27.40	0.16
Muscovite	6.94	-
Magnesiochloritoid	0.46	-
Anatase	0.94	-
Rutile	1.74	-
Hematite	2.95	-
Magnetite	0.60	-
Dolomite	-	1.27
Amorphous	58.90	-

Table 3 Mineral compositions of tested cement

Mineral Compositions (% by weight)	PCC
C_3S	58.57
C_2S	9.67
C_3A	4.83
C_4AF	9.30
Lime	0.03
Portlandite	1.43
Quartz	0.03
Gypsum	0.70
Bassanite	2.63
Anhydrite	0.27
Calcite	11.80
Dolomite	0.13

The water to binder ratio used for shrinkage tests was fixed at 0.35. In this study, 4 mixes were produced including PCC as a control mix. The other 3 mixes were binary and two ternary mixtures. The two ternary mixes differed in the ratio of CC to LP, which was 1:1 and 2:1. The amount of 10% limestone powder presented in the hydraulic cement is incorporated to the total limestone powder portion when calculating the ratio. The tested mix proportion is shown in Table 5.

Table 4 Physical properties of tested binders

Physical Properties	PCC	CC	LP
Specific gravity	3.06	2.62	2.7
Median particle size (μm)	10.53	14.03	6.79

Table 5 Tested mix proportions

Mixture ID	Binders (% by weight)			Ratio of CC to LP
	PCC*	CC	LP	
PC100	100	0	0	-
PC70CC30	70	30	0	4:1
PC70CC19LP11	70	19	11	1:1
PC70CC25LP5	70	25	5	2:1

*PCC included about 10% of limestone powder

2.2 Methodology

(1) Mixing

Paste samples were selected for the experiment to explicitly investigate the shrinkage behavior of the tested mixes. Specimen preparation was done according to ASTM C157/C157M [14]. Bar molds with the size of 25×25×285 mm^3 were used. Two stainless steel studs were placed at both ends of the mold for each bar specimen. The binder was mixed with PCC using a mechanical mixer at room temperature and was placed into the mold simultaneously. Precautions were taken throughout the preparation to minimize moisture loss from the paste samples. The specimens were stored in controlled environment at 25±1°C and 55-70% relative humidity (%RH) and were demolded after 18 hours. The temperature of 25±1°C and relative humidity of and 55-70%RH were implemented to simulate the hot weather in Thailand. The samples for both autogenous and total shrinkage tests were prepared at the same time.

(2) Autogenous shrinkage

After demolding, initial measurements were taken using a Vernier caliper and a length comparator. To prevent water and moisture exchange, the specimens were sealed with a multi-layer covering comprising two layers of aluminum tape, followed by ten layers of plastic wrap, and finished with two layers of sellotape (Fig. 1). The initial weight of each specimen was recorded to confirm no moisture exchange occurred during the experiment, with a weight difference limit of 0.03%. Four specimens were cast for PC100 mixture, and 6 specimens were cast for each of the other mixtures. The sealed specimens were then stored on racks under controlled conditions of 25±1°C and 55-70%RH.

Shrinkage evaluation involved measuring length changes using a length comparator (Fig. 2). The calculation for autogenous shrinkage is the difference between initial length and length at testing period of interest divided by the initial length. The obtained results were averaged from four or six specimens.

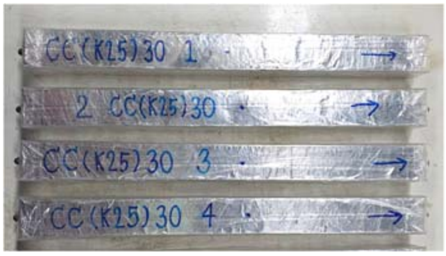

Fig. 1 Specimens of autogenous shrinkage test

Fig. 2 Length comparator

Fig. 3 Specimens of drying shrinkage test

(3) Length change during water curing and drying shrinkages

Four specimens were cast for each mixture. The same specimens were used for both length change and weight change experiments, and the results were averaged. Initial measurements were taken using a Vernier caliper and a length comparator after the specimens were demolded. Initial weight was also taken at the same time. The specimens were cured in tap water at 25±1°C for 6 days (until reaching an age of 7 days) and then placed on racks for air drying. The samples were stored at 25±1°C and 55-70%RH. After 77 days for PC100, PC70CC30, and PC70CC25LP5 mixes and after 70 days for PC70CC19LP11 mix, the room RH was changed to be 40-55%RH due to humidity control issues. Length measurements were conducted daily for the first 14 days, every other day until the age of 28 days, and weekly until the age of 98 days. The period of measurement was the same as autogenous shrinkage test. Weight of samples was recorded throughout the test period to evaluate weight gain during water curing and loss during drying. The specimens for drying shrinkage test are shown in (Fig. 3).

3. RESULTS AND DISCUSSIONS

3.1 Autogenous Shrinkage

(1) Effects of calcined clay

Fig. 4 presents the autogenous shrinkage results for the four mixtures from 0 to 98 days. From 0 to 5 days, the control mixture showed slightly higher autogenous shrinkage compared to the other mixtures. Subsequently, the shrinkage increased gradually and continued to develop throughout the experimental period. Mixtures containing CC exhibited greater autogenous shrinkage than the control mixture after 5 days. The binary mixture with CC showed approximately 200 microns more shrinkage than the control from 28 to 98 days. Even with clay containing a low kaolinite content (25%), the autogenous shrinkage is likely to increase as reported in previous study utilizing clay with 40% kaolinite content [13]. This increased shrinkage is likely due to self-desiccation associated with the CC. The water vapor sorption isotherm results for PCC and CC samples, presented in Fig. 5, clearly indicate that CC with a high specific surface area absorbs more water compared to the PCC. The BET results by water adsorption confirm the significantly higher surface area of CC relative to PCC, (35.53 and 10.52 m^2/g, respectively). The water adsorption on the high surface area of clay before the reaction may contribute to more significant self-desiccation of mixtures with CC, leading to larger autogenous shrinkage.

(2) Effects of ratio of calcined clay to limestone powder

The inclusion of LP in the mixtures resulted in an even greater increase in autogenous shrinkage compared to mixtures partially replaced with CC alone. From 0 to 6 days, ternary mixtures showed similar shrinkage to binary mixture with very slightly lower value. However, after 7 days, the autogenous shrinkage of the ternary mixtures increased significantly, with the 1:1 CC-to-LP ratio producing the highest autogenous shrinkage. These findings suggest that LP does not mitigate the issue of autogenous shrinkage.

Limestone calcined clay mixtures incorporated CC with higher kaolinite content also demonstrated higher autogenous shrinkage than cement-only mixture as reported by Nguyen et al. (2022), Afroz et al. (2023), Hay et al. (2022), and Du and Pang (2020) [6] - [8], [15]. Nguyen et al. (2022) reported that LC^3 mixture using high-grade CC generated pore refinement within the system, with higher cumulative volume of micropores, gel pores, and medium capillary pores compared to cement-only mixture. Therefore, there was more capillary tension produced from LC^3, which caused higher autogenous shrinkage. Similarly, Afroz et al. (2023) found that LC^3 mixtures containing CC with a kaolinite content of approximately 47.5% exhibited abundant hydration products, contributing to pore refinement [7].

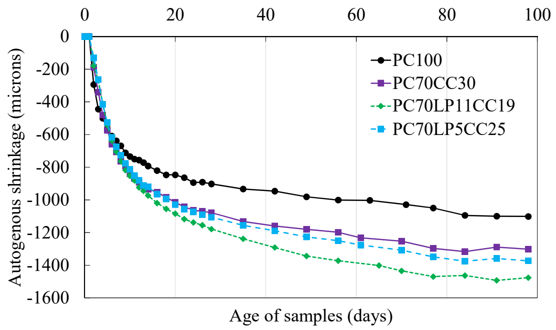

Fig. 4 Autogenous shrinkage of tested paste

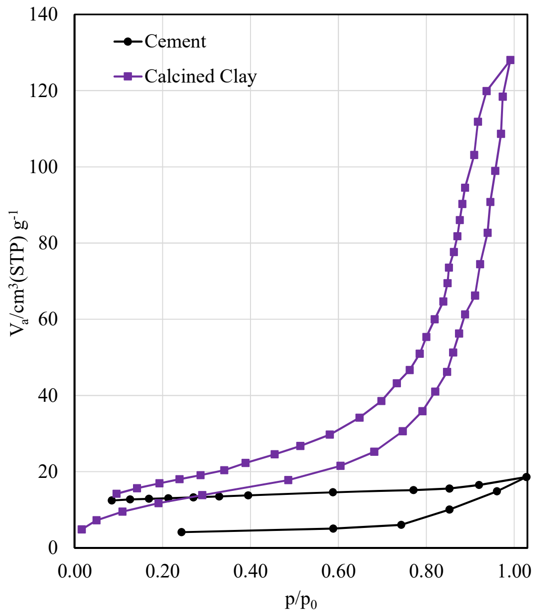

Fig. 5 Water vapor sorption isotherm of tested paste

Du and Pang reported pronounced autogenous shrinkage in LC^3 mixtures containing CC with 60% kaolinite from as early as 1 day, which was attributed to the high pozzolanic reactivity of CC. Additionally, the high surface area of the CC resulted in water adsorption on the clay surface, thereby reduced the effective water available for hydration reactions, exacerbating autogenous shrinkage. This was followed by synergistic reaction between CC and LP, contributing to later-stage shrinkage [15].

Sudsawong similarly stated the fast reaction of CC as the cause of high autogenous shrinkage of CC mixtures when compared to cement-only mixture. However, in his study, CC mixture exhibited higher autogenous shrinkage than CC-LP mixtures after 70 days, which contrasts with the findings of the current study. The effects of LP on autogenous shrinkage require further clarification in future research.

Kaolinite content of CC significantly affects the pozzolanic reaction within the LC^3 system. Higher kaolinite content results in higher compressive strength gain and faster pore refinement as reported by Avet and Scrivener [16]. Accordingly, kaolinite content of clay may influence autogenous shrinkage as well. Further investigations are recommended to elucidate this relationship.

3.2 Length Change During Water Curing and Drying Shrinkage

(1) Length change during water curing

Length and weight changes during water curing were recorded daily and are presented in Fig. 6 and 7. During this period, the control mixture gradually expanded with weight gain until an age of 7 days. This expansion can be attributed to the recovery of shrinkage in water after demolding due to the swelling of calcium silicate hydrate (C-S-H) caused by water absorption [17]. During water curing, water penetrated into its unsaturated pores from the surface, further contributing to expansion. After 1 day of water submersion, the mixtures that contain CC also expanded significantly, however, shrinkage began at 3 days even though weight gain with water absorption. As shown in Fig. 4, incorporation of clay is likely to increase autogenous shrinkage, which can cause shrinkage even in water.

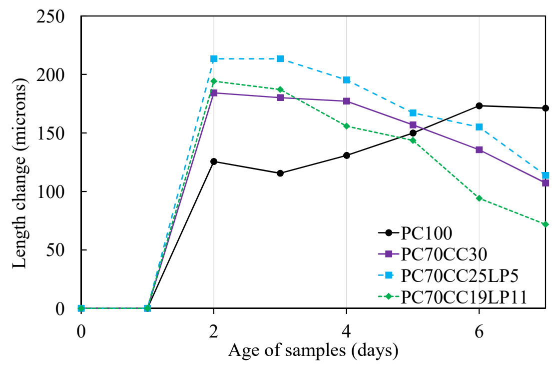

Fig. 6 Length change of tested paste in water during curing

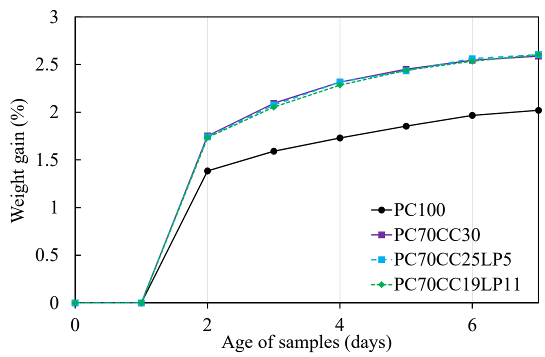

Fig. 7 Weight gain of tested paste in water during curing

(2) Effects of calcined clay on drying shrinkage

Fig. 8 shows drying shrinkage results of mixtures from ages of 7 to 98 days. At 7 days, when the samples were exposed to air-dry condition of 25±1°C and 55-70%RH, all mixtures exhibited significant shrinkage. The control mixture shrank gradually and exhibited lower drying shrinkage than other mixtures from 8 days until 16 days. However, it showed the maximum drying shrinkage after 16 days. This drying shrinkage was reduced when CC was used in the mixtures. This reduction can be attributed to the shrinkage that had already occurred during the water submersion phase, as discussed in the previous section. The early-age shrinkage observed in mixtures incorporated clay indicates that a portion of total shrinkage had already taken place, leaving less potential for subsequent long-term shrinkage. This behavior is different from that of the conventional cement paste of PC100. Consequently, the magnitude of shrinkage of mixtures with calcined clay during drying period is lower than that of PC100 mixture.

Another possible reason for low drying shrinkage observed in CC mixtures is the formation of C-A-S-H, resulting from the reaction between alumino silicates in CC and calcium hydroxide produced during cement hydration [2]. Segawa et al. (2024) reported that an increase quantity of C-A-S-H can contribute to a reduction in drying shrinkage [18]. However, in contrast to the findings of this study, Sudsawong reported a higher total shrinkage in mixtures containing CC with 40% kaolinite content compared to cement-only mixture [13]. This discrepancy points out the need for further investigation into the influence of C-A-S-H on drying shrinkage, particularly when incorporating CC with varying kaolinite contents.

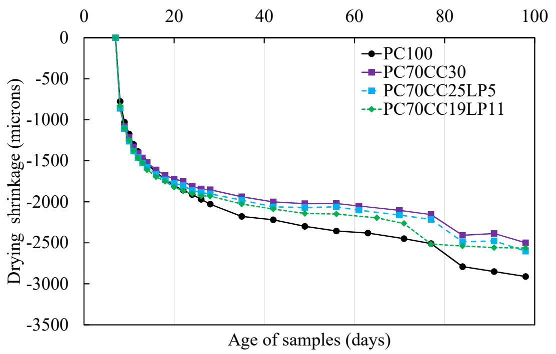

Fig. 8 Drying shrinkage of tested paste

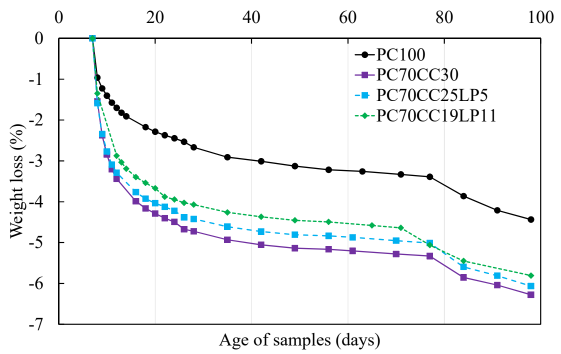

Fig. 9 Weight loss of tested paste with time

Fig. 9 illustrates the time-dependent weight loss of drying shrinkage samples. The CC mixtures exhibited approximately 1.5 times greater weight loss compared to the cement-only mixture. Among the mixtures, the CC binary mixture demonstrated the highest weight loss but the smallest amount of drying shrinkage. This substantial weight loss suggests that CC samples possess a high volume of coarse pores (macropores) in paste matrix and/or a high specific surface area of clay, allowing more water to disperse from the pores or on the surfaces of CC particles, compared to that from PC100 samples.

The hypothesis regarding macropores of CC mixture may be due to the use of CC with low kaolinite content in this study that results in low pore refinement of paste matrix [16]. Further investigation into the pore structures of CC mixtures with a low content of kaolinite is necessary to verify these findings.

(3) Effects of ratio of calcined clay to limestone powder on drying shrinkage

After 7 days, mixtures containing additional LP exhibited smaller shrinkage compared to control mixture. However, when compared to CC binary mixture, CC-LP mixtures showed higher drying shrinkage with the mixture having a CC-to-LP ratio of 1:1 showing the largest drying shrinkage, the same as observed in autogenous shrinkage results. Additionally, shrinkage observed during water curing may reduce the overall shrinkage during drying, similar to the behavior of CC-only samples. The mechanism of increase shrinkage when mixing LP with CC should be elaborately studied further.

The weight loss graph in Fig. 9 illustrates that the mixture with CC-to-LP ratio of 2:1 had larger weight loss than the 1:1 ratio mixture. This implies that LP may play a significant role in weight loss of samples. When a higher proportion of LP was used in the mixture, weight loss decreased, and vice versa. The results indicate that the pore refinement can be achieved by incorporating LP as reported in the previous studies [6] - [7].

4. CONCLUSIONS

In this study, autogenous and drying shrinkage of CC with kaolinite content of 25% and LP from Thailand were investigated. The conclusion drawn from the results are as follows:

(1) Paste mixtures incorporating CC showed larger autogenous shrinkage compared to the control mixture.
(2) The addition of LP did not reduce autogenous or drying shrinkage compared to CC-PCC mixture.
(3) Mixtures containing both CC and LP demonstrated lower drying shrinkage than the control mixture.
(4) Shrinkage was observed in mixtures with CC even during water submersion prior to the drying process, which mitigated their subsequent drying shrinkage.
(5) While CC mixtures exhibited the lowest drying shrinkage, they experienced the highest weight loss.
(6) Further studies on the kaolinite content, pore structure, and C-A-S-H products of CC mixtures are recommended to validate the observed shrinkage behavior.

ACKNOWLEDGEMENT

The first author would like to extend sincere gratitude toward Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan for being awarded the Monbukagakusho scholarship at Saitama University. The authors are sincerely thankful to the support by the Japan Concrete Institute (JCI) under the JCI research grant FY2023 (Keisuke Takahashi). The authors acknowledge the great support received from Prof. Somnuk Tangtermsirikul of the Construction and Maintenance Technology Research Center, Sirindhorn International Institute of Technology (SIIT), Thammasat University and SCG Co., Ltd.

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