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Influence of Limestone Powder Particle Size and Content on Portland Cement Paste Properties

Cheng-Xuan Yu[1], Wei-Chien Wang[1*], Hoang-Trung-Hieu Duong[2], and Jia-Chen Xue[1]

[1]Department of Civil Engineering, National Central University, Taoyuan, Taiwan

[2]Can Tho University of Technology, Can Tho City, Viet Nam

*Corresponding author (a654.joy@gmail.com)

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ABSTRACT

The purpose of this study was to investigate the effects of different particle sizes and contents of limestone powder (LSP) on the compressive strength and workability of ordinary Portland cement (OPC) paste. Three types of LSP with different specific surface areas (SSA) were used to replace OPC in proportions ranging from 0 to 40%. Both compressive strength and flow experiments were conducted, and the results were analyzed using regression analysis. The findings were further corroborated by X-ray diffraction analysis. The experimental results show that the higher the SSA and the smaller the particle size, the worse the workability. Notably, when the content of LSP is less than 20%, the influence of LSP particle size on compressive strength and workability is not significant. However, when it exceeds 20%, the greater the SSA of LSP, the smaller the particle size, and the smaller the reduction in compressive strength. According to the result, the LSP-F has the optimal performance in the higher replacement, especially at the 20% replacement.

1. INTRODUCTION

Limestone powder (LSP), already one of the raw materials used to make ordinary Portland cement (OPC), is more readily available to cement plants than other alternative cementitious materials. LSP is softer and more grindable than clinker, resulting in higher fineness when mixed and ground. This ensures a uniform particle size and allows for particle size adjustment according to specific needs. Over the past decade, the addition of LSP as an auxiliary cementitious material to replace cement has gained widespread acceptance (Ijaz et al., 2024)

As early as 1990, a study investigated the use of LSP as a minor addition in cement (<5%) (Hooton et al., 2007). In 2008, the Portland Cement Association conducted a comprehensive review of the literature and permitted the inclusion of LSP in ASTM C150 up to 5%. Subsequently, in 2012, ASTM C595 introduced a new type of cement called Portland limestone cement (PLC), allowing LSP content up to 15% of the cement mass. Additionally, European standards (EN 197-1) permit the addition of LSP up to 35%, which is currently the highest allowance in global standards. The permissible dosages of LSP according to current global standards are illustrated in Figure 1 (Dhandapani et al., 2019).

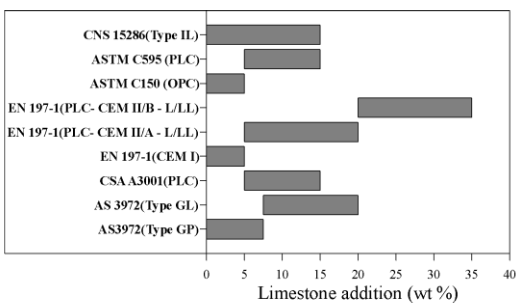

Figure 1. Allowable limit for LSP addition

According to the study by Wang et al. (2018), LSP produces four effects: filler, nucleation, dilution, and chemical. The filler effect occurs when the particle size of LSP is finer than that of cement particles, effectively filling the voids in the concrete, improving its compactness, and thus enhancing its durability. The nucleation effect means that the surface of LSP particles, which is rich in Ca^{2+} ions, provides nucleation sites for the early formation of hydration products. The smaller the particle size of LSP, the more nucleation points are available, accelerating the hydration reaction, the heat of hydration, the nucleation of calcium hydroxide, and improving the early strength of the concrete. Additionally, during the hydration process, $CaCO_3$ dissolves, releasing Ca^{2+} ions into the solution, which aids in the precipitation of silicate hydration products, thus increasing the hydration degree of the cement (Wang et al., 2018).

The dilution effect refers to the partial reaction of LSP due to the low alumina content in the cement. Therefore, substituting LSP for cement reduces the cement content in the concrete, thereby reducing the hydration peak of C_3S, decreasing the amount of hydration products generated, increasing the porosity of the concrete, and reducing its mechanical properties. Although EN 197-1 allows for the addition of up to 35% LSP to cement used in concrete, according to Elgalhud et al. (2016), adding more than 15% to 25% LSP expands the dilution effect, resulting in excessive porosity of the specimen, which in turn affects its safety and durability. The chemical effect involves the reaction of $CaCO_3$ in LSP with aluminate to form semi-carbon aluminate (H_c) and mono-carbon aluminate (M_c), depending on the amount of carbonate present, as shown in Equation (1) (IEA, 2018).

$$C_3A + CaCO_3 + CH + H \rightarrow C_3A.CaCO_3.H_{12}(M_c) \quad (1)$$

The effects primarily depend on the particle size and amount of LSP. It is worth noting that LSP does not produce a pozzolanic reaction and, therefore, does not generate CSH gel. This study focused on the effects of different particle sizes and content of LSP on the compressive strength and workability of paste. Additionally, it explored the impact of the maximum addition amount allowed by national standards of various countries on engineering performance.

2. MATERIAL AND METHOD

2.1. Material

This research employed Portland cement Type 1 (Taiwan Cement Company, Taipei, Taiwan), with the chemical composition of the cement outlined in Table 1. The LSP utilized in this study is delineated in detail in Table 2 and Figure 2.

Table 1. Chemical and mineralogical compositions of cement

Chemical composition	Wt (%)	Mineralogical composition	Wt (%)
SiO_2	19.45	C_3S	49.5
CaO	63.79	C_2S	23.3
Al_2O_3	5.48	C_3A	4.7
Fe_2O_3	3.46	C_4AF	10.0
MgO	1.63		
SO_3	3.19		
f-CaO	0.74		
Ca/Si	3.28		
I,L.*	1.7		

**I.L. is the abbreviation for loss on ignition.*

Table 2. Chemical compositions of LSP

Chemical composition	Wt(%)
SrO	0.119
ZnO	0.009
Fe_2O_3	0.164
TiO_2	0.073
CaO	96.966
K_2O	0.03
Cl	0.027
SO_3	0.112
SiO_2	0.724
Al_2O_3	0.253
MgO	1.461
Na_2O	0.062

Table 3. The Property of LSP

ID	SSA* (m^2/kg)	Size(d_{50})(μm)
LSP-C	277.5	33.49
LSP-M	278	25.3
LSP-F	505	12.6

**SSA is the specific surface area*

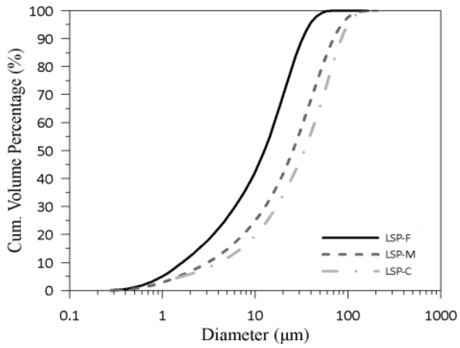

Figure 2. Particle size distributions of LSP

2.2. Mixture considered

Referring to the national standards of the United States (ASTM C595), Canada (CSA A3001), Taiwan (CNS 15286), and Australia (AS 3972), this study will set the LSP addition amount of 0%~20%, and focus on the impact of every 5% LSP added on the engineering properties of the paste, and include the maximum addition amount (35%) permitted by the European (EN 197-1) to discuss its reduction of engineering performance. It is important to note that the ratio set by the specification is the mass ratio. For the experiment specimen ID of this research, please refer to Table 4.

Table 4. The binder ratio for the cement paste in this research

unit: vol %

Specimen ID	OPC	LSP-C	LSP-M	LSP-F
PC	100	-	-	-
PLC-C5	95	5	-	-
PLC-C10	90	10	-	-
PLC-C15	85	15	-	-
PLC-C20	80	20	-	-
PLC-C40	60	40	-	-
PLC-M5	95	-	5	-
PLC-M10	90	-	10	-
PLC-M15	85	-	15	-
PLC-M20	80	-	20	-
PLC-M40	60	-	40	-
PLC-F5	95	-	-	5
PLC-F10	90	-	-	10
PLC-F15	85	-	-	15
PLC-F20	80	-	-	20
PLC-F40	60	-	-	40

2.3. Experiment methods and analysis

The effect of LSP on cement hydration was investigated by evaluating the flowability and compressive strength results.

2.3.1. Flow test

This test evaluates the effect of the LSP on the workability of the cement paste. The flow test was conducted following the ASTM C230.

2.3.2. Compressive strength test

This test evaluates the effect of the LSP on the cement paste mechanical property at 3, 7, and 28 days. The compressive strength test was conducted following the ASTM C109. The Specimen's size is 5 cm × 5 cm × 5 cm.

2.3.3. X-ray diffraction (XRD) analysis

XRD analysis was performed on BRUKER D2 PHASER equipped with a LYNXEYE XE-T detector. After 3 and 28 days, take the internal fragments of the test specimen after the compressive strength test, grind them into a powder that can pass the #200 sieve, place them in a vacuum oven (76 Hg/mm) at 45 degrees Celsius, dry them for more than 72 hours, and then take out the powder for XRD analysis, and set the scanning range of the instrument to be 10°~30° 2θ. Step scanning was used with a scan speed of 2°/min and a sampling interval of 0.02° 2θ.

2.3.4. Regression analysis

Regression analysis was compared with the control group, based on a Bivariate polynomial equation, like eq. (2), x is the LSP content, y is the LSP particle size, $f(X,Y)$ is the results of each test, was used to carry out regression analysis, and a 50*50 contour plot was made to explore the interaction of LSP filling effect, nucleation effect, and chemical effect on the performance of PLC under different particle sizes.

$$f(x,y) = \sum_{i=0}^{N} \sum_{j=0}^{N} a_{ij} x^i y^j \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Flow test

As depicted in Figure 3, when substituting OPC with LSP-C, the higher the content, the better the flowability, with paste flow increasing by 4% for every 5% addition. Conversely, substituting OPC with LSP-F slightly reduces the workability of the cement paste. This is attributed to the high SSA of LSP, which tends to retain water molecules, thereby reducing the effective water-cement ratio and diminishing cement paste flowability. Furthermore, LSP-M has minimal impact on workability. These findings help to explain the varying assessments of

LSP influence on paste workability found in different studies.

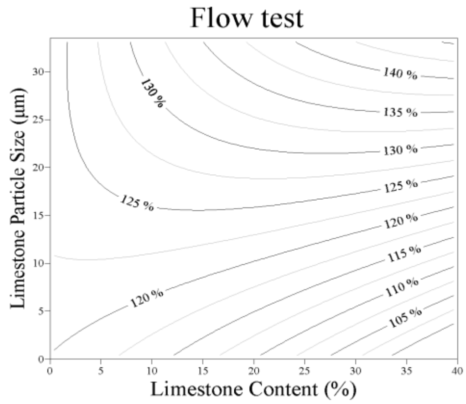

Figure 3. Regression analysis of the flow test

3.2. Compressive strength

The compressive strength is mainly affected by the LSP content and particle size. With the increase in LSP addition, the dilution effect becomes more pronounced, resulting in a decrease in strength. According to the experiment results, as shown in Figure 4, for the strength of the specimen with LSP-C, the strength is reduced with the content, and the overall strength is reduced by 5% for every 5% LS-C added. For LSP-C and LSP-M specimens, the addition amount within 15% has no significant effect on the compressive strength, but the substitution amount exceeds 15%, and its strength is reduced to more than 75%. LSP-F specimens, due to the smaller SSA, can provide more nucleation sites, promote the precipitation of hydration products, and improve the mechanical properties under the action of filling effect and nucleation effect, and LSP-F still shows good mechanical properties when added to 20%. The experiment results are in accordance with ASTM C595 for compressive strength at the age of 3 days, 7 days, and 28 days.

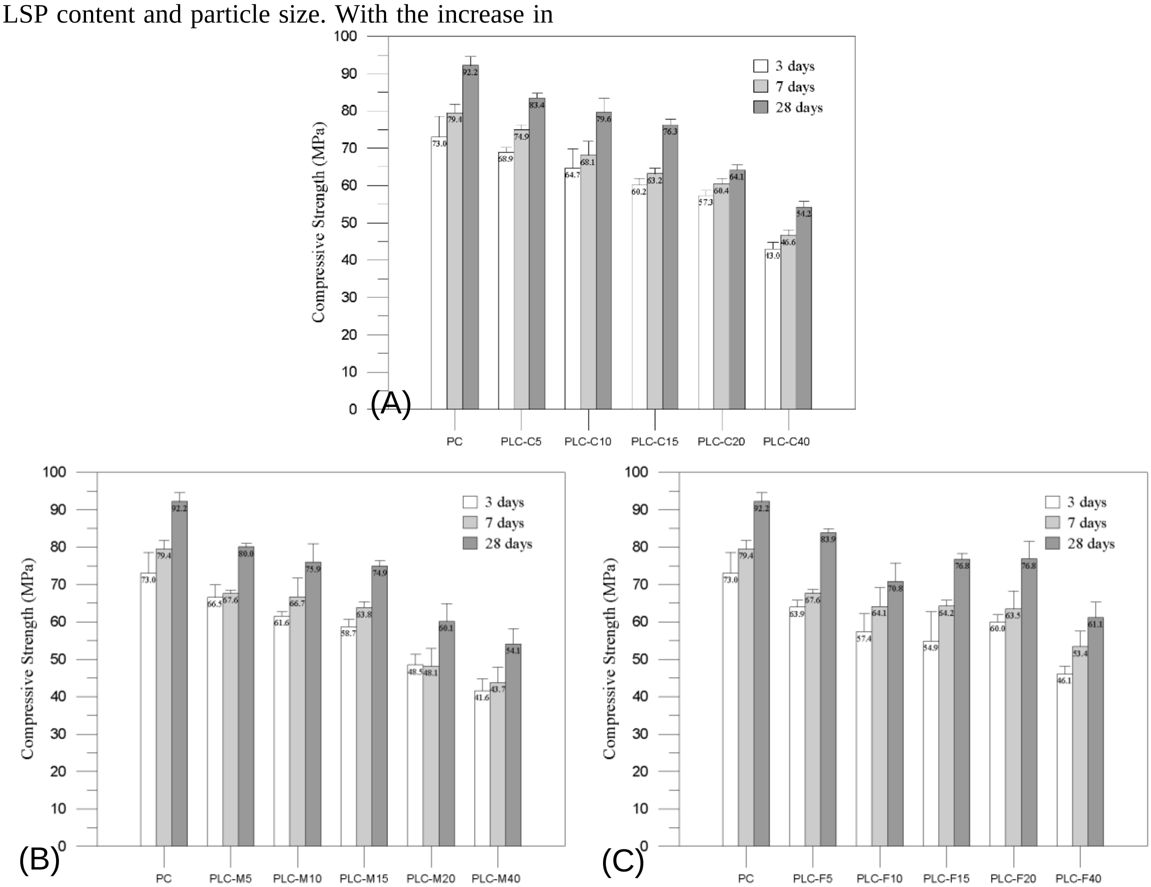

Figure 4. The compressive strength result

(A)The PLC-C group, (B)The PLC-M group, (C)The PLC-F group

3.2.1. Relative of the compressive strength

This section will reference the findings of Vance et al. (2013) to address the lack of smaller particle-sized LSP (0.7 µm, 3 µm, 15 µm) in this study. Combined with the compressive strength test results from this research, we will explore the influence of different LSP particle sizes and content on compressive strength and its associated trends.

The compressive strength result will be compared with the control group, and the relative strength will be shown as a percentage (%) to explore the effect of the addition of LSP on the mechanical performance of Portland cement paste. According to the regression analysis (Figure 5), at 3 days, when the LSP addition is less than 20%, or the LSP particle size is less than 5µm, it has minimal impact on the paste strength, maintaining compressive strength at over 75%. At 7 days, with LSP addition under 15% or particle size below 10µm, strength remains largely unaffected, with compressive strength maintained at over 75%. At 28 days, when LSP addition is below 17% or particle size is under 7µm, strength is similarly maintained at over 75%. Overall, adding 15% LSP in line with ASTM and CNS specifications preserves strength above 75%, while the AS specification's maximum allowable addition of 20% keeps strength above 70%. However, adding 35% LSP according to EN specifications significantly reduces strength to around 60%.

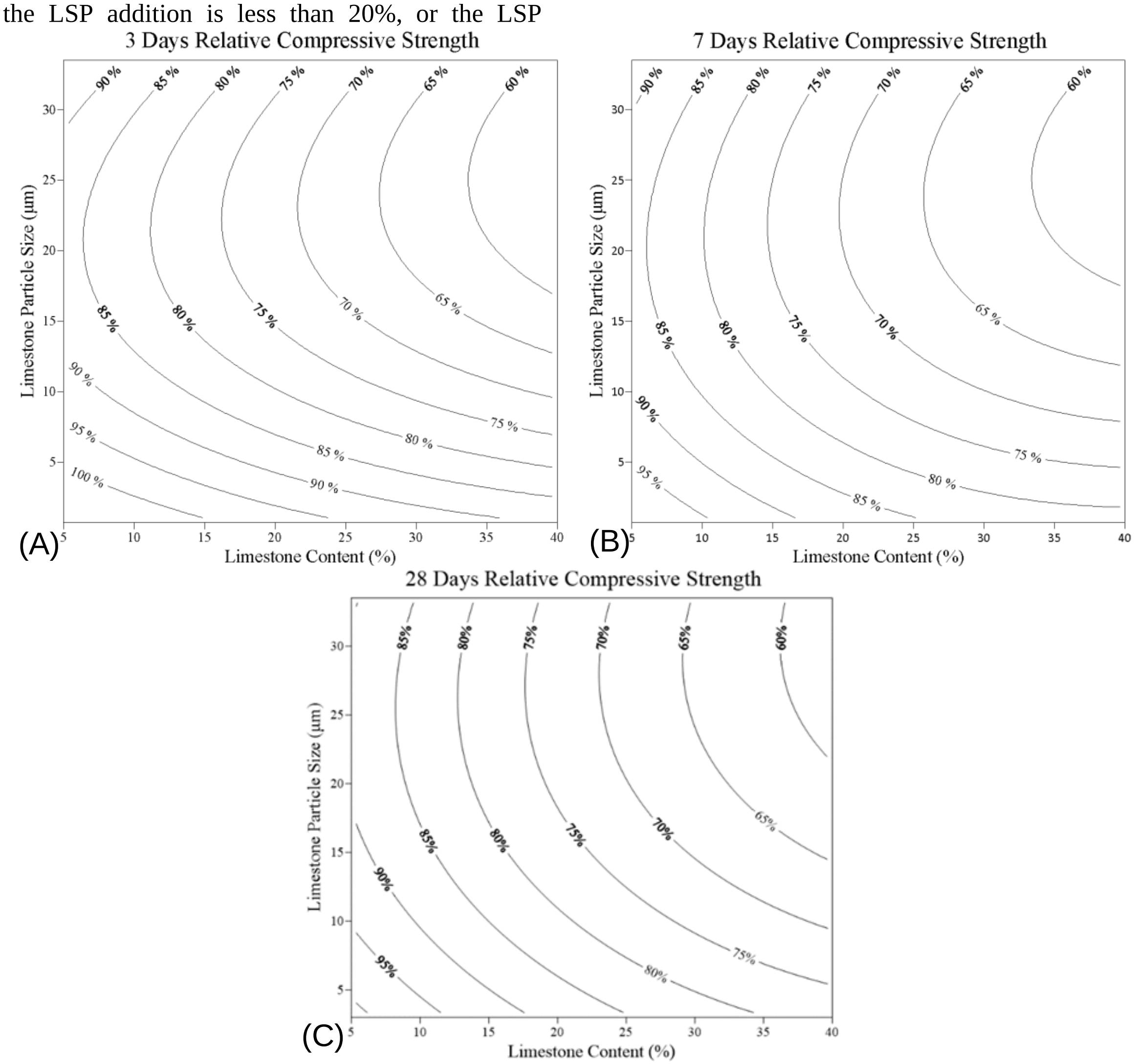

Figure 5. Regression analysis of the compressive strength

(A)3 days, (B) 7 days, (C) 28 days

3.3. XRD analysis

According to the XRD analysis (Figure 6), it is evident that PLC-F40 exhibits the highest calcium hydroxide content in both early and later stages. This confirms that smaller LSP particle sizes provide more nucleation sites for hydration products, enhancing the nucleation effect and resulting in higher compressive strength of the specimen. The XRD analysis further verified that smaller LSP particles intensify the chemical reaction, producing more Mc. With a density of 1.98 g/cm³, Mc is lower than other hydration products (IEA, 2018), which aids in filling the pores in concrete. Therefore, the smaller LSP particle sizes could improve the mechanical properties and durability of the specimen.

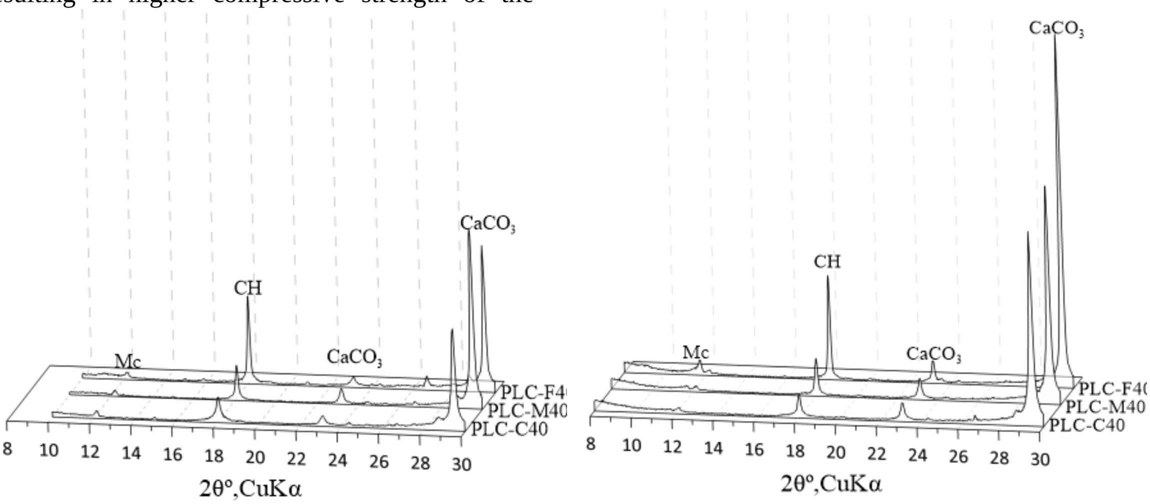

Figure 6. XRD pattern

(A)3 days (B) 28 days

3.4. Discussion

The results of the flow test (Section 3.1) show that when the particle size of LSP is larger, the available water increases, resulting in better flowability. Conversely, when the particle size of LSP is smaller, a higher content will trap water, slightly reducing the workability of the paste. This is similar to the findings of Nair et al. (2020) and Vance et al. (2012).

The results of the compressive strength test (Sections 3.2 and 3.3) indicate that overall, as the amount of LSP added increases, the dilution effect becomes more pronounced, and the strength decreases more. The results of this experiment align with Dhandapani et al. (2021), indicating that when LSP substitution is below 30%, the filler and chemical effects can balance the dilution effect, resulting in no significant strength reduction. However, when LSP addition exceeds 30%, the strength of specimens in most studies drops below 75%. When LSP is added in proportions exceeding 15% to 25%, the dilution effect increases, leading to excessive porosity in the specimen, thus affecting the material's safety and durability. Consequently, both ASTM and CNS currently limit the maximum LSP content to 15%.

However, it can be observed that when the replacement amount of LSP-F reaches 20%, it does not show a significant reduction in strength like other coarser LSPs. According to the regression analysis results in Section 3.3, when the particle size of LSP is less than 5μm, it still exhibits excellent mechanical properties even when the replacement amount reaches 40%. As the particle size of LSP decreases, the effect of LSP content on strength becomes less significant. Therefore, it is recommended to consider relaxing the restrictions on the addition of fine particle size LSP to further reduce carbon emissions from PLC.

4. CONCLUSION

In this study, the workability and mechanical properties of the cement paste were examined in relation to the impacts of different particle sizes and the content of the limestone powder (LSP). The following conclusions could be made as the primary research findings:

– The greater the fineness of the LSP and the smaller the particle size, the worse the workability, especially as content increases. Conversely, lower LSP fineness and larger particle size improve workability as content increases.

– If the content of LSP is less than 15%, the effect of LSP particle size on compressive strength and workability is not significant. However, when it exceeds 15%, the higher the fineness of LSP and the smaller the particle size, the less the reduction in compressive strength.

– According to regression analysis, when the LSP addition is less than 20%, the compressive strength of the specimen decreases by approximately 5% to 10% for each 5% increase in content. Additionally, adding less than 15% LSP or using LSP with a median particle size(d_{50}) less than 5μm has minimal effect on the compressive strength of the paste.

– X-ray diffraction results indicate that smaller LSP particle size correlates with more intense nucleation and chemical effects, resulting in higher compressive strength in the test samples.

This study confirms that the smaller the particle size of LSP, the smaller the strength reduction caused by replacing Portland cement. When using LSP with smaller particle size, the additional amount can be increased without significantly affecting the overall performance, and improve its carbon reduction benefits, providing a reference for relaxing the standard increase ratio. Future research could extend considerations to durability properties. Additionally, exploring the composite effect of other supplementary cementitious materials with LSP could help mitigate the dilution effect caused by LSP and increase its content, thereby improving the engineering performance and carbon reduction effect of PLC.

5. CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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