

ORIGINAL ARTICLE



PCE Superplasticizers for Calcined Clay Blended Cements – Challenges and Solutions

Jiaxin Chen¹ | Ran Li¹ | Karl-Christian Thienel² | Johann Plank¹

Correspondence

Prof. Dr. Johann Plank
Technical University of Munich
Lichtenbergstraße 4
85748 Munich
Email: johann.plank@tum.de

¹ Technical University of Munich,
Munich, Germany

² University of the Bundeswehr
Munich, Neubiberg, Germany

Abstract

A high content of metakaolin in calcined clay blended cement has a positive effect on the early strength development, however, it also leads to a poor workability. Moreover, slump retention is more difficult to achieve in this system than in OPC or other composite cements. In this study, several approaches were investigated to achieve fluidizing ability of mortars prepared from composite cements holding 30 wt. % of calcined clay with varying amounts of metakaolin (~ 23 wt.%, ~ 51 wt.%). First, it was found that the slump retaining performance of a common industrial ready-mix type HPEG PCE rapidly decreases when the content of metakaolin increases. Furthermore, a combination of the ready-mix HPEG PCE and a retarder (sodium gluconate) which is commonly applied in ready-mix concrete, also fails to improve fluidity retention in calcined clay blended cement with a high level of metakaolin, hence highlighting the difficulty of slump retention for such cements. To mitigate this problem, a unique admixture based on the combination of a precast type HPEG PCE and a novel PCE-LDH nanocomposite is introduced. Mortar tests reveal that the high water-reducing (precast) type HPEG PCE and the PCE-LDH nanocomposite enables to achieve a remarkable improvement in fluidity retention of such calcined clay blended cements.

Keywords

Calcined clay, PCE superplasticizers, Low-carbon Cement, LDH nanocomposite, Workability

1 Introduction

Thermally activated (calcined) clays (CCs) appear to present the most promising approach to reducing the clinker factor in cement and thus reducing its CO₂ footprint [1-4]. However, large-scale high quality applications of such cements will occur only when the properties of concretes prepared from those cements can be controlled in the fresh and hardened state through the addition of chemical admixtures including polycarboxylate (PCE) superplasticizers [3, 5-7]. For them, the challenge is to fluidize such concretes at dosages that are known for other composite cements such as fly ash, slag, or limestone blended cements.

Unfortunately, the high specific surface area and the considerable internal porosity of individual calcined CCs can lead to poor workability [5, 8]. This negative effect is more pronounced when the calcined clay incorporates a high metakaolin content [8]. Moreover, in practical application, it has been observed that flow retention, a key requirement for ready-mixed concrete, is more difficult to achieve in calcined clay blended cements than in ordinary Portland cement (OPC).

Conventional technologies for achieving slump retention in OPC are based on the encapsulation and delayed addition of PCE superplasticizers, a more detailed description can be found in the previous literature [9]. The intercalation of PCE superplasticizers into layered double hydroxides (LDHs)[10] is considered as a promising new approach to improve fluidity retention in calcined clay blended cements. For this purpose, PCE-LDH nanocomposites were synthesized via hydration of tricalcium aluminate (C₃A) in the presence of PCEs, it was hoped to achieve superior slump retaining times via anion exchange with the sulfate from the pore solution [10, 11].

To elucidate whether PCE-LDH could solve the urgent problem of inadequate slump retention in calcined clay blended cements, in this study, two low-carbon calcined clay blended cements were utilized, with the calcined clay samples incorporating low (~23 wt. %) and high (~51 wt. %) metakaolin content in their raw clays respectively. First, to demonstrate the negative impact of calcined clay on slump retention, a conventional industrial ready-mix type PCE known for its superior workability retention in OPC was tested individually and in combination with a re-

tarder (sodium gluconate) in neat OPC and composite cement system. The fluidity retention behavior of PCE and PCE/retarder was investigated via isothermal heat flow calorimetry. In the next step, the fluidizing ability of a novel PCE-LDH nanocomposite was studied to examine whether it could provide sufficient slump retention in low-carbon calcined clay blended cements.

2 Materials and methods

2.1 Cement

The cement used in this study was an ordinary Portland cement CEM I 42.5 R. Its phase composition as determined by Q-XRD employing Rietveld refinement is presented in Table 1. This cement exhibits a density of 3.13 g/dm⁻³ (Helium pycnometry) and a d₅₀ value of 18.1 μm (laser granulometer, Cilas 1064, Cilas Company, Marseille, France).

Table 1 Phase composition of the cement sample CEM I 42.5 R.

Phase	wt. %
C ₃ S, monoclinic	59.55
C ₂ S, monoclinic	11.08
C ₄ AF, orthorhombic	10.07
C ₃ A, cubic	4.88
C ₃ A, orthorhombic	2.06
Anhydrite (CaSO ₄)	2.59
Dihydrate (CaSO ₄ •2H ₂ O)	3.09
Hemihydrate (CaSO ₄ •0.5H ₂ O)	0.10
Calcite (CaCO ₃)	2.34
Dolomite (CaMg(CO ₃) ₂)	0.97
Periclase (MgO)	0.53
Portlandite (Ca(OH) ₂)	0.78
Arcanite (K ₂ SO ₄)	0.22
Quartz (SiO ₂)	0.42
Free lime (Rietveld)	0.62
Free lime (Franke)	0.70
Total	100

2.2 Calcined clay samples

In this paper, two calcined clay samples different metakaolin contents were selected: CC 23 (23 wt.%), and CC51 (51 wt.%), the composition of their raw clays and calcined clays samples were determined by quantitative XRD measurements. Table 2 provides the respective contents.

Table 2 Mineralogical composition of the raw and the calcined clay samples, as determined by XRD including Rietveld refinement

Mineral phase	Raw clay	Cal. clay	Raw clay	Cal. clay
	CC23	CC23	CC51	CC51
	(wt. %)	(wt. %)	(wt. %)	(wt. %)
Kaolinite	22.6	-	51.3	-
Illite - Smectite	31.8	4.6	19.7	-
Muscovite	4.7	2.2	18.1	5.2
Quartz	16.2	20.0	10.3	13.8
Rutile	0.3	-	0.5	0.3
Muscovite HT	-	-	-	18.6
Chlorite	5.6	0.4	-	-
Carbonates	8.5	0.6	-	-
Sulfates	-	1.6	-	-
Anatase	1.8	-	-	-
Ore	0.9	1.1	-	-
Other minerals	7.6	9.1	-	-
Amorphous	-	60.8	-	62.2
Total	100	100.4	99.9	100.1

2.3 Admixtures

2.3.1 PCE superplasticizers

An industrial commercial ready mix type of PCE polymer (HRM) based on HPEG macromonomer containing hydrolyzing ether provided by JILIN Chemical Industrial (Jilin, China) was employed to investigate the effect of hydrolyzing ether on slump retention performance on calcined clay blended cement. HRM exhibits a specific anionic charge amount of 915 μeq/g, which signifies its high ester content.

Additionally, an industrial precast-type HPEG PCE (JILIN Chemical Industrial, Jilin, China) which is designed such as to provide high initial fluidity (the so-called "high water-reducing" type, WRP) was used. Its specific anionic charge amount in 0.1 M NaOH was found at 1805 μeq/g, this indicates a particularly high anionic charge density, which is characteristic for precast-type PCEs.

2.3.2 Retarder

As retarder, sodium gluconate (>99% purity, SG) supplied by the China Academy of Building Research (CABR, Beijing) was applied.

2.3.3 Ca–Al-LDH nanocomposite

The preparation of Ca–Al-PCE-LDH nanocomposite was prepared via rehydration of C₃A according to the method described by Li et al. [9]. During the synthesis, the self-prepared methacrylate ester PCE 45PC6 was used.

2.4 Mortar tests

The time-dependent dispersing performance of the polymers was ascertained via mortar tests, which were performed according to DIN EN 196-1 standard [12]. For all mortar samples, the water-to-binder ratio (w/b) of 0.4, and the binder-to-sand ratio of 3:1 was kept constant. The mixing procedure was as follows: First, 450 g of OPC (or OPC/CC binder) was added to a mixing bowl containing 180 g of deionized (DI) water and different dosages of PCE/SG/PCE-LDH. Immediately after the binder was added, the mixer (Toni Technik, Berlin, Germany) was started with a mixing speed of 140 rpm for 30 s. Next, the standard sand was added within the next 30 s at the same mixing speed. After the addition, the mixer stirred at 285 rpm for another 30 s. During a 90s pause, a spoon was used to scrape the mixture from the bowl edges to ensure a homogeneous mortar. Then the mixing was continued at 285 rpm for another 60 s. After the mixing process, the mortar was filled up in a Vicat ring (height of 60 mm, top diameter of 80 mm, and bottom diameter of 100 mm) which was placed on the spread flow table (FORM+TEST, Riedlingen, Germany). Followed by a 15 times shock the spread was measured twice with a caliper vertically, and averaged. The time-dependent spread flow measurement was measured every 30 min after the binder contact with water until the spread flow was less than 12 cm. After each measurement, the mortar was transferred back into the mixing bowl and covered with a wet towel to avoid any desiccation of the cement mortar. Prior to each spread flow test, the cement mortar was stirred for 2 min with a speed of 285 rpm.

2.5 Isothermal heat flow calorimetry

To investigate the effect of the HRM-PCE and HRM-PCE/sodium gluconate combination on the hydration of calcined clay blended cements, heat flow calorimetric measurements were carried out using a TAM Air Calorimeter (TA Instruments, Järfälla, Sweden). For the measurements, 4 g of binder with and without 0.7 % bwob. HRM-PCE or combination of 0.7 % bwob. HRM-PCE/0.3 % bwob. SG was weighed into 20 mL glass ampoules and mixed with DI water. Individual time-dependent heat release was prepared at a w/b ratio of 0.5 for OPC, a w/b ratio of 0.59 for the OPC:CC23, and a w/b ratio of 0.82 for the OPC:CC51, the ratio was fixed to achieve a comparable paste spread flow of 18 ± 0.5 cm in the mini-slump tests. Next, the ampoules were capped, homogenized in a wobblers for 2 min, and then placed in the calorimeter. Measurements were carried out until the release of heat from the hydration reaction subsided completely.

3 Results

3.1 Slump retention ability of conventional ready-mix PCE and PCE/sodium gluconate combination

Sodium gluconate, a common auxiliary retarding admixture to prolong workability time, is usually employed in combination with PCE superplasticizers to obtain fluidity retention in cement and concrete [13, 14]. To investigate the impact of calcined clay on the time-dependent fluidity of mortars admixed with the HRM-PCE, the time-dependent mortar flow of neat OPC and calcined clay blended cements was measured.

As shown in Figure 1, in neat OPC, a dosage of 0.7% bwob. of HRM-PCE reached a spread flow of 19 cm, and the initial fluidity is maintained for ~ 60 min. With the combination of an additional 0.03% bwob. of SG (such a rate is commonly used in practice) the fluidity retention time was prolonged to 90 min, which indicates the well-known synergistic effect between HRM-PCE and the retarder [9]. The slump retention effect of sodium gluconate has been extensively studied previously and can be attributed to the postponed formation of ettringite [14].

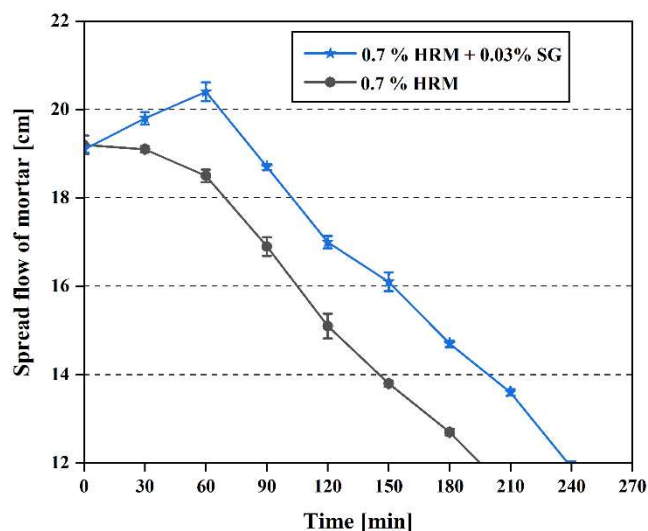


Figure 1 Fluidity retention of mortars prepared from neat OPC admixed with HRM, HRM/sodium gluconate combination

The evolution of mortar flow over time of composite cements holding 30 wt. % of CC23 and CC51 respectively is illustrated in Figure 2. As is evident there, the synergistic effect of HRM-PCE and the sodium gluconate retarder is still effective in OPC:CC23 blended cement, however, in composite cement with a high metakaolin content (OPC:CC51), the slump retention ability of HRM-PCE and HRM-PCE/SG combination was severely hindered. Furthermore, in the presence of high levels of metakaolin, the effectiveness of sodium gluconate as an auxiliary slump retainer is almost completely lost.

These results indicate that flow retention is difficult to achieve in composite cements with a high level of metakaolin when using conventional approaches that are effective for OPC. However, a solution to this problem is crucial for the large-scale application of calcined clay blended cements in the future.

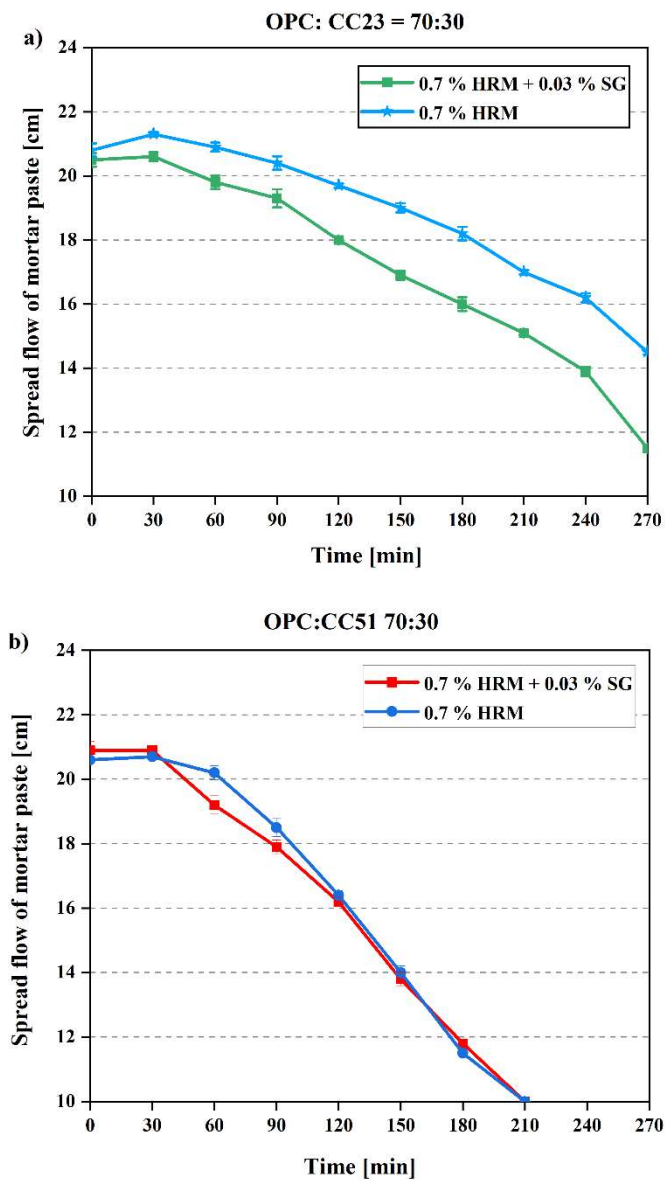


Figure 2 Fluidity retention of mortars prepared from a) OPC:CC23 70:30 b) OPC:CC51 70:30 blend admixed with HRM, HRM/sodium gluconate combination

3.2 Mechanistic study via hydration kinetics measurements

To understand the reason behind the negative impact of metakaolin in calcined clay, the hydration of the OPC and calcined clay cement were studied with HRM-PCE and HRM-PCE/SG retarder combination via isothermal heat flow calorimetry.

As shown in Figure 3, with the addition of HRM-PCE into OPC and OPC:CC23, the induction period was prolonged by ~ 20 h, and the combination of HRM-PCE/SG retarder leads to a further extension of ~ 3 h. However, in OPC:CC51 blended cement, the hydration curve of HRM-PCE and HRM-PCE/sodium gluconate retarder was almost similar, and there was no apparent delay of acceleration period after the addition of SG, which signifies that the ineffectiveness of SG in calcined clay blended cement with a high amount of metakaolin.

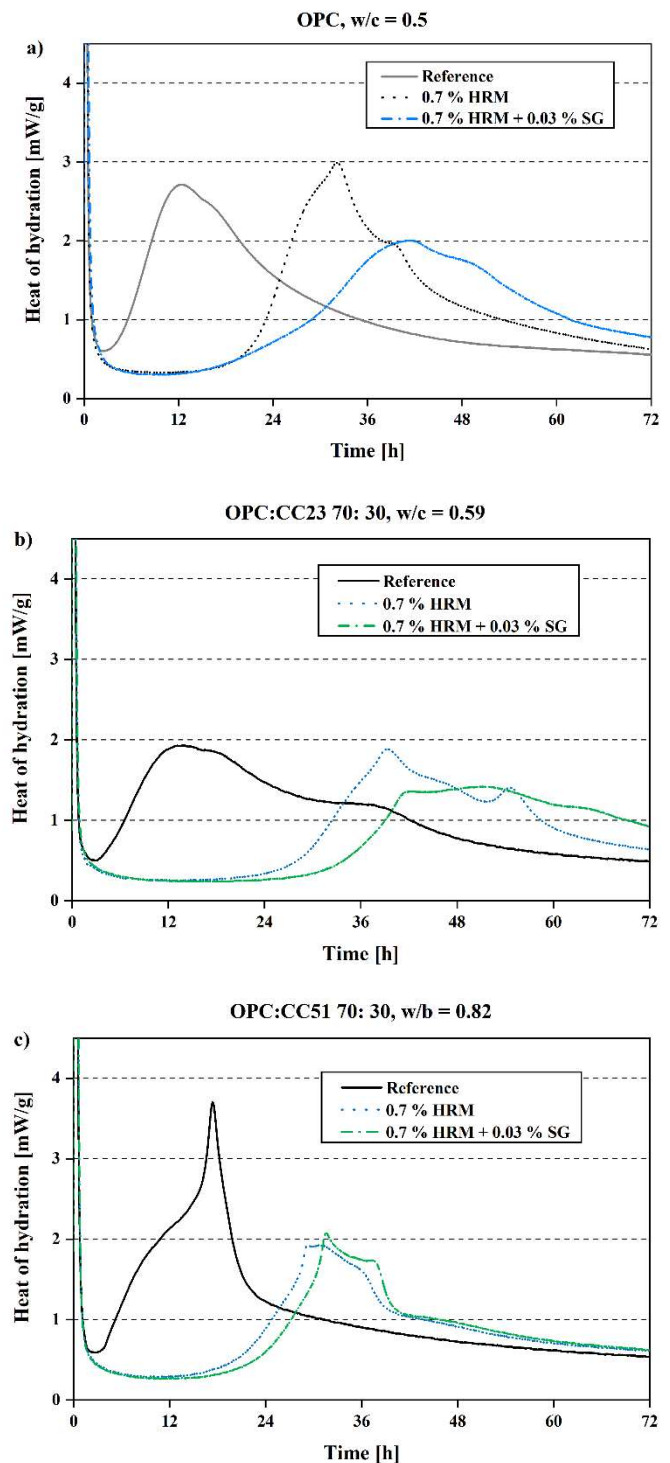


Figure 3 Time-dependent evolution of the hydration heat released from pastes prepared from a) neat OPC b) OPC:CC23 70:30 c) OPC:CC51 70:30 blend admixed with HRM, with or without sodium gluconate (w/b ratio = 0.4).

3.3 Performance of PCE-LDH nanocomposite

According to an earlier study [15], the hydration of C_3A produces layered double hydroxides which can intercalate anionic superplasticizers in between their $[Ca_2Al(OH)_6]^+$ main layers. In this study, Ca-Al-PCE-LDH admixture was introduced as a new type of slump retainer that captures the PCE in the interlayer region and gradually releases the PCE during cement hydration via anionic exchange with sulfate anions.

As the PCE-LDH cannot provide instant fluidity, a commercially available precast type HWR-PCE was applied to generate the initial dispersion, and the dosage of HWR-PCE was adjusted to achieve an initial spread flow of 19 ± 0.5 cm in spread flow tests. Time-dependent mortar flow was recorded and the results are illustrated in Figure 4, it is obvious that although the addition of HWR-PCE yields a high initial flow at low dosage, however, it is unable to maintain sufficient workability over time. This negative trend became even worse with the increasing content of metakaolin incorporated in calcined clay blended cements. Hence, to improve slump retention, the mortars holding HWR-PCE were additionally treated with 0.4 % bwob. of the PCE-LDH nanocomposite, and the time-dependent fluidity was recorded every 30 minutes. The results are displayed in Figure 5.

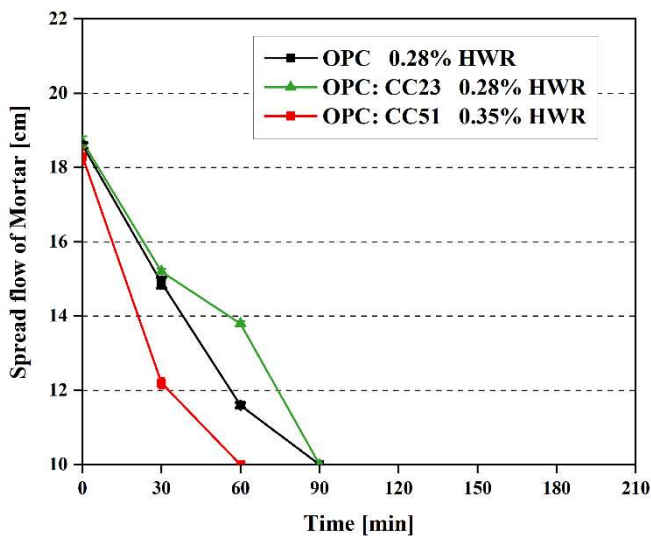


Figure 4 Fluidity retention of mortars prepared from neat OPC or OPC/CC blends admixed with WR-PCE

It is surprising that the addition of the PCE-LDH nanocomposite to the OPC:CC23 composite cement enables it to obtain similar slump retention as in the OPC mortar. However, in OPC:CC51 blended cement, the PCE-LDH admixture fails to achieve a comparable flow retaining ability at the same dosage of PCE-LDH admixture. It indicates that as the content of metakaolin increases, the effectiveness of the PCE-LDH admixture gradually diminishes. Li et al. [9] revealed that this problem can be resolved by a higher dosage of PCE-LDH nanocomposite.

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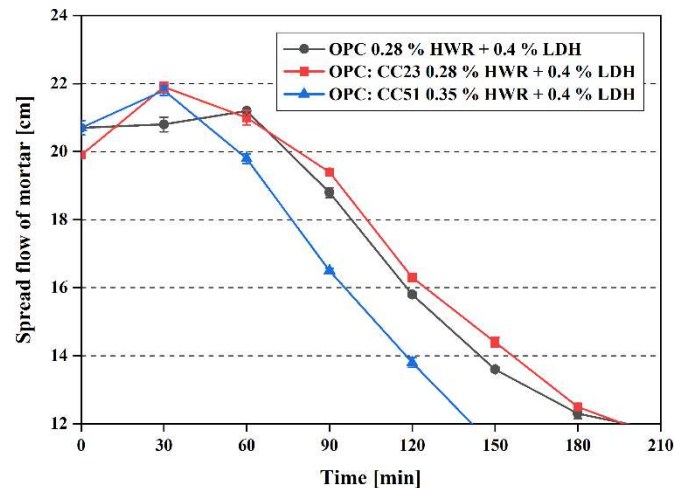


Figure 5 Fluidity retention of mortars prepared from neat OPC or OPC/CC blends admixed with WR-PCE and Ca-Al-PCE-LDH nanocomposite

It can be concluded that the combination of a precast-type WRP-PCE and a PCE-LDH admixture can successfully overcome the flow retention problem caused by the incorporation of calcined clay with a high metakaolin to cement.

4 Conclusion

In this study, the fluidity retention behavior of different admixtures in OPC and low-carbon calcined clay blended cements holding varying metakaolin contents were investigated. A comparison between a commercial slump-retaining HPEG PCE and a novel PCE-LDH nanocomposite was performed in composite cements holding different content of metakaolin (23 wt.%, 51 wt.%).

First, it was found that it was extremely difficult to achieve adequate flow retention after partial replacement of OPC with calcined clay holding a high content of metakaolin. In such composite cement, conventional ready-mix HPEG PCE and its combination with sodium gluconate retarder exhibit limited effectiveness on slump retention. Second, the combination of precast-type WRP and the novel PCE-LDH admixture allows achieving the desirable slump retention as required in practical applications.

In conclusion, PCE-LDH admixture is a viable solution to the lack of slump retention capacity of calcined clay blended cements, and enables a more widespread application of such low-carbon cements

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