*- Technical Paper -*

# OPTIMIZING GRAPHENE OXIDE DISPERSION FOR STRENGTH ENHANCEMENT IN CEMENT MORTARS

Vignarajah JANANI [*1], Yogarajah ELAKNESWARAN[*2], Yuya YODA[*3], and Ryoma KITAGAKI[*4]

ABSTRACT

This study investigated the optimization of graphene oxide (GO) dispersion using three types of polycarboxylate-ether-based superplasticizers (PS), which were introduced at different times during ultrasonication. Notably, introducing PS after 30 minutes of ultrasonication enhanced GO dispersion and stability, as evidenced by zeta potential and particle size analysis. Properly dispersed GO in cement mortar resulted in an increase in compressive strength. These findings highlight the importance of selecting the appropriate dispersion method to achieve stronger and more durable cement-based materials.

Keywords: Cement mortar, Graphene Oxide, Dispersion, Stability, Superplasticizer

## 1. INTRODUCTION

Nanotechnology is a prominent topic in recent research to get major effective solutions regarding its application in cementitious materials, which have wide-ranging implications in tackling today's key challenges of durability, mechanical strengths, and sustainability in the construction industry [1]. Among various nanomaterials, graphene oxide (GO) is one of the most efficient additives due to its unique properties, such as a high surface area of 700-1500 $m^2/g$, a high elastic modulus of 210-470 GPa, tensile strength of 130 GPa [2,3] and reactive functional groups like hydroxyl, carboxyl, epoxy, and carbonyl [1]. These properties enhance GO to interfere with cement hydration products, increasing its hydration kinetics and improving microstructural properties [4]. The hydration of ordinary Portland cement (OPC) results in calcium hydroxide (CH) and other hydration products, along with the calcium silicate hydrate (C-S-H), which is the predominant strength-giving component of the concrete. The functional groups of GO serve as a nucleation site for the C-S-H reaction [5] by facilitating the formation of dense hydration products that refine microstructure, improving both physical and mechanical properties.

Incorporating GO in a cementitious matrix reduces workability due to its high surface area and hydrophilic nature, increasing water demand and decreases flowability [6]. Even though GO is stable while suspended in aqueous solutions due to electrostatic repulsion and its hydrophilic nature, it is challenging to disperse effectively in the cement pore solution [7]. The presence of high concentrations of ions ($Na^+$, $K^+$, $OH^-$ and $Ca^{2+}$) in the pore solution undermines this stability [8–10] and, therefore, leads to poor or uneven dispersion of GO. This instability leads to agglomeration driven by van der Waals forces and surface charge interactions. Agglomeration of GO reduces its reinforcing capacity, creating defects and weak zones in the cement matrix [10]. Therefore, ensuring proper dispersion of GO within the cementitious system is essential to maximizing its impact on hydration and mechanical properties.

Ultrasonication is the most common physical approach to dispersing GO in aqueous solutions. However, these dispersions generally persist for a short time, after which they tend to re-agglomerate because of the inherent tendency of GO sheets to aggregate. This re-agglomeration resulted from the cross-linking of calcium ions ($Ca^{2+}$) in the cementitious environment, which facilitates the restacking of GO sheets [11]. In the chemical approach, the use of superplasticizers has emerged as an effective solution [12]. Superplasticizers, especially polycarboxylate ether (PCE) - based types of admixtures, are very common in the use of cement-based materials for their application to enhance workability and lower the water-to-cement ratio without sacrificing mechanical performance [13]. These admixtures work through electrostatic repulsion and steric hindrance mechanisms, wherein superplasticizer molecules adsorb onto the particle surface, preventing aggregation and facilitating the formation of a stable and homogeneous dispersion [14]. Superplasticizers stabilize GO particles under alkaline conditions, improving their dispersion within the cement matrix and mitigating the adverse effects of agglomeration. The combination of GO and superplasticizer in a cement matrix promotes uniform dispersion of GO particles and enhances their interaction with cement hydration products, accelerating hydration and improving pore structure and microstructural integrity [10]. Thus, the most efficient dispersion and stabilization of GO can be accomplished through the combination of physical and chemical approaches.

Researchers have attempted to enhance the dispersion of GO in the cement matrix using the

*1 Graduate School of Engineering, Hokkaido University, JCI Student Member
*2 Associate Prof., Division of Sustainable Resources Engineering, Hokkaido University, JCI Member
*3 Engineering Researcher, Shimizu Corporation, Shimizu Institute of Technology, JCI Member
*4 Professor, Division of Architecture, Hokkaido University, JCI Member

aforementioned combined approaches. For instance, Chuah et al. investigated the effect of different surfactant treatments on GO dispersion in cement composites [15]. Similarly, Yan et al. compared different kinds of superplasticizers to optimize the GO dispersion and improve the mechanical properties of cement mortar [11]. In another study, Fonseka et al. investigated the effect of GO properties, superplasticizer type, and dispersion techniques on the mechanical properties of GO-added concrete [16]. Despite the enormous potential advantages of combining these approaches, we need to understand their synergistic performance further, particularly in a highly alkaline environment.

This study focuses on optimizing GO dispersion in cement mortars by preparing GO-PS suspensions using different types of Polycarboxylate-ether-based superplasticizers and evaluating their dispersion quality through zeta potential and particle size measurements. The most effective dispersion method will then be applied to incorporate GO into cement mortars to investigate its influence on compressive strength. By establishing a link between dispersion quality and mechanical performance, this work aims to provide insights into the synergistic effects of GO and superplasticizers, paving the way for developing advanced cementitious materials.

## 2. Materials and Methods

### 2.1 Raw materials

The GO used in this study was in the form of slurry and was procured from Ceylon Graphene Technologies (Pvt) Ltd, Sri Lanka. Three types of Polycarboxylate-ether-based superplasticizers (PS) were employed to aid the dispersion of GO in deionized water. PS A and PS B are polycarboxylic acid ether-based superplasticizers with density ranges of 1.02–1.12 g/cm³ and 1.03–1.12 g/cm³, respectively, while PS C is a modified polycarboxylate with a density of 1.11 g/cm³. Ordinary Portland Cement (OPC) obtained from the Japan Cement Association was selected as the primary binding material, and its chemical composition is tabulated in Table 1.

Table 1 Chemical composition of the OPC

| Parameter | Percentage (%) |
|---|---|
| $SiO_2$ | 21.27 |
| $Al_2O_3$ | 5.54 |
| $Fe_2O_3$ | 2.90 |
| CaO | 64.72 |
| MgO | 1.51 |
| $SO_3$ | 1.82 |
| $Na_2O$ | 0.23 |
| $K_2O$ | 0.39 |
| $TiO_2$ | 0.28 |
| $P_2O_5$ | 0.45 |
| MnO | 0.05 |
| Cl | 0.022 |
| Ignition loss | 0.58 |

### 2.2 GO-PS suspension preparation

An appropriate amount of GO slurry and deionized water was transferred into a beaker and subsequently homogenized at 3000 rpm for 15 minutes to achieve uniform dispersion. To prevent water evaporation during ultrasonication, the beaker containing the GO suspension was sealed with parafilm. PS was introduced at different times during the ultrasonication process for three samples: in the first sample, PS was added before ultrasonication; in the second sample, PS was added after 15 min of ultrasonication; and in the third sample, PS was added after 30 minutes of ultrasonication, as illustrated in Fig.1. Following the addition of PS, the mixture was further homogenized for 5 minutes at 3000 rpm to ensure homogeneous mixing. All samples underwent ultrasonication for 30 cycles (1 min of ultrasonication followed by 1 min of rest) at a frequency of 40 kHz and a power output of 400 W to achieve optimum dispersion and stability of the GO suspension.

### 2.3 Sample preparation for zeta potential and particle size measurement

To evaluate the stability and dispersion of GO in PS solution, as well as its interactions with cement pore solution, zeta potential and particle size measurements were performed using a Zeta potential and Particle size Analyzer (ELSZ-1000, Japan). Zeta potential indicates the electrostatic stability of GO, while particle size analysis enables the identification of potential agglomeration, ensuring optimal performance and compatibility within cementitious systems. For these measurements, suspensions were prepared at concentrations of 0.1 g/L and 0.5 g/L for zeta potential and particle size analysis, respectively. The average value for each suspension was determined through three repeated measurements.

### 2.4 Preparation of cement pore solution

The preparation of early cement pore solution was as follows: First, the cement and water were put together in a mixer with a water-to-cement ratio of 10:1 and stirred for 1 h at high speed. Then, the fresh cement paste was centrifuged at 10000 rpm for 5 min. The supernatant clear solution was collected using a membrane filter as a cement pore solution.

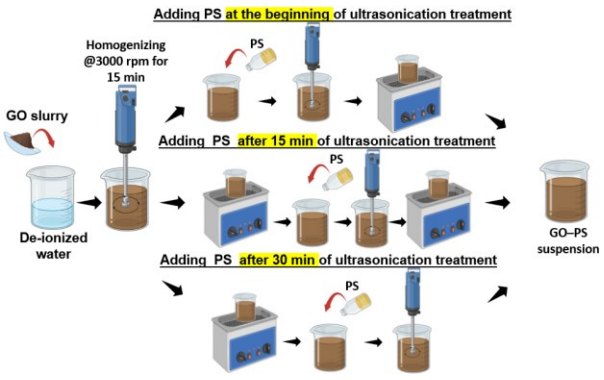


Fig.1 Schematic illustration of the preparation of GO-PS suspension

### 2.5 Preparation of GO-modified cement mortar

The incorporation of GO in the preparation of cement mortar was done through a well-designed protocol for precision and reproducibility. All mixtures maintained a constant water-to-cement (w/c) ratio of 0.4, and GO was added at a dosage of 0.02% by weight of cement. Initially, cement and premixed GO-PS suspension were mixed at low speed for 30 sec in a planetary-type mixer (Hobart N50 5-Quart mixer). Then, sand was introduced into the mixture and mixed at low speed for 30 sec and high speed for 30 sec for complete homogenization. The mixing was momentarily halted, and then the surface of the mixture was cleared using a spatula. Following this, high-speed mixing occurred for 1 minute to ensure the mixture was well-mixed. The fresh mortar is cast in cylindrical moulds measuring 50 mm in diameter and 100 mm in height in 2 layers and is subjected to 20 seconds of vibration in each layer to eliminate any air bubbles and promote uniformity. The samples were then covered with a thin plastic film to prevent water loss by evaporation and put in a controlled curing environment at a constant temperature of 20 ± 2°C. After being moulded after 24 hours, samples were stored under conditions of temperature 20 ± 2°C for 7 days before being subjected to compressive strength testing.

## 3. RESULTS AND DISCUSSION

### 3.1 Zeta potential analysis

The graph in Fig 2(a) illustrates the impact of the PS introduction time on the zeta potential. According to this figure, all GO-PS suspensions show negative zeta potential values, indicating the adsorption of negatively charged functional groups from the PS onto the GO surface. The zeta potential becomes increasingly negative as the PS introducing time progresses from 0 to 30 minutes for all PSs. This effect can be attributed to ultrasonication, which promotes improved exfoliation of the GO sheets [11] and enhances the exposure of reactive sites on their surface. The increased availability of these sites facilitates greater PS adsorption, resulting in high negative electrostatic repulsion and steric hindrance to balance the Van der Waals forces [17], leading to better dispersion of GO.

Focusing on Fig.2(b), it demonstrates the time-dependent stability of GO and GO-PS suspensions over 24 hours, with PSs introduced after 30 minutes of ultrasonication. GO without PS exhibits significant fluctuations in zeta potential. This fluctuation may be attributed to the lack of stabilizing agents, leading to instability in its dispersion. On the other hand, GO with PS suspensions shows comparatively smaller fluctuations, owing to the electrostatic repulsion mechanism that sustains stability and ensures uniform dispersion of GO [16]. GO-PS C exhibits the most stable zeta potential over time with minimum fluctuations, which indicates that PS C likely forms strong and consistent electrostatic or steric interactions with GO. Although GO-PS A also shows a relatively small range of fluctuation, the absolute zeta potential values of GO-PS C remain consistently higher (less negative) than the

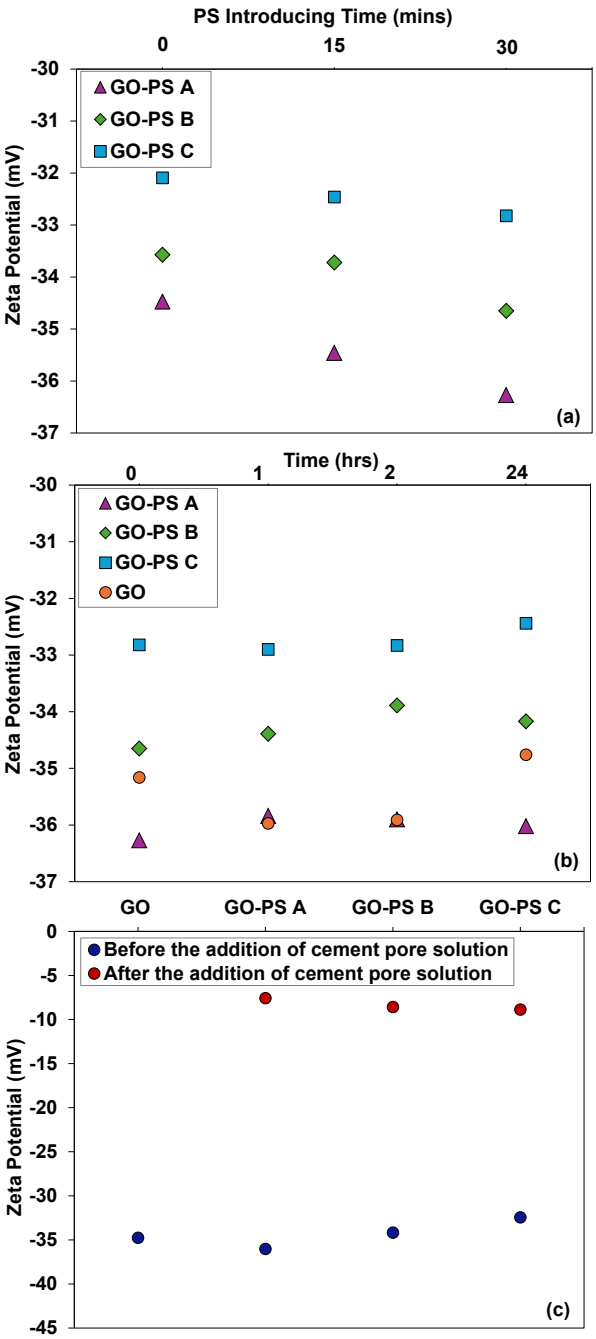


Fig.2 Zeta potential variation of GO with and without PS (a) Effect of PS introducing time, (b) Stability over time, and (c) Impact of cement pore solution addition

others, indicating a more stable electrostatic environment. GO-PS B, in contrast, exhibits slightly larger variations, which may suggest weaker or slower stabilization. The differences among the GO-PS suspensions likely arise from the molecular structure and charge density of the respective PSs.

As shown in Fig.2(c), adding cement pore solution significantly reduces the zeta potential. This decrease is primarily attributed to the cement pore solution's high ionic strength, which contains abundant cations such as $Ca^{2+}$, $Na^{+}$, and $K^{+}$. These cations adsorb onto the negatively charged functional groups on the

surface of GO or GO-PS suspensions, neutralizing the surface charge and reducing the zeta potential. For GO without PS, this addition promotes agglomeration due to the cross-linking action of $Ca^{2+}$ ions. These ions link functional groups at the edges of GO sheets together to yield larger clusters [18]. In contrast, GO-PS suspension may still carry sufficient negative charges and maintain stability due to the steric hindrance provided by the PS, which shields the GO surface from excessive cation adsorption and prevents agglomeration even under conditions of high ionic strength [19].

### 3.2 Particle size analysis

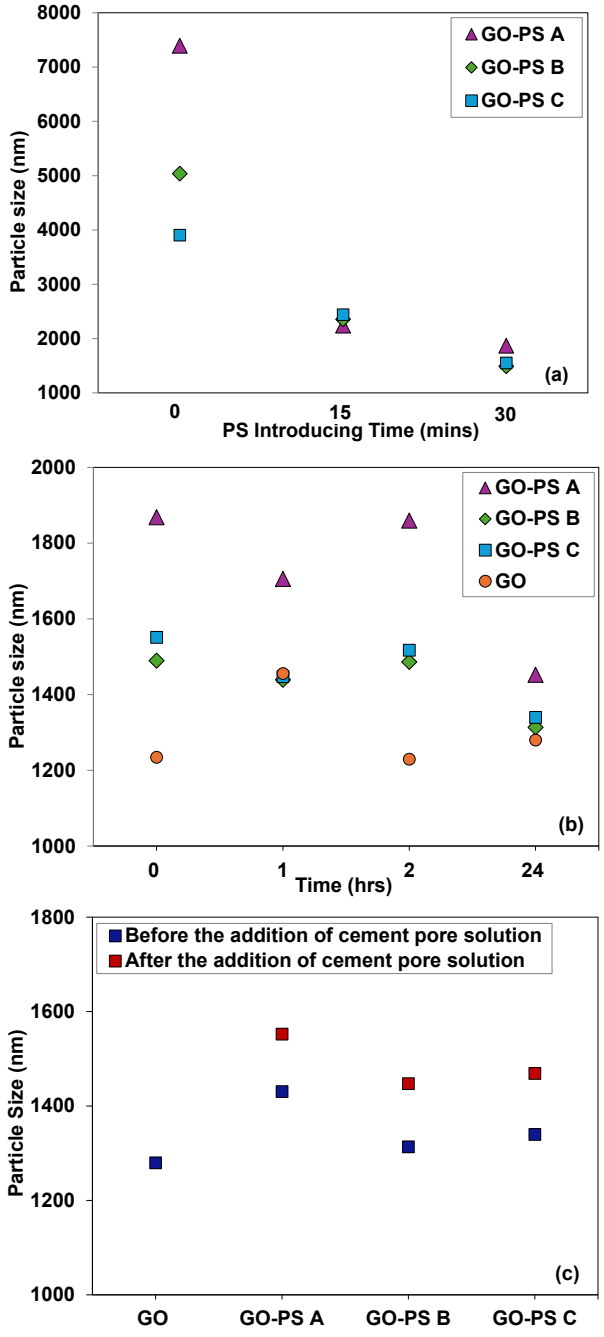


Fig.3 Particle size variation of GO with and without PS (a) Effect of PS introducing time, (b) Stability over time, and (c) Impact of cement pore solution addition

The results of particle size analysis correlate with the zeta potential results. Analyzing trends in Fig.3 (a) confirms that delaying the PS introducing time during the ultrasonication treatment promotes better exfoliation of the GO sheets. This allows more reactive sites for PS adsorption and increases electrostatic repulsion, leading to better dispersion and reduced particle size. Fig.3 (b) depicts the stability of GO suspensions with time. GO without SP shows poor stability because of weak electrostatic repulsion. GO-PS suspensions exhibit good stability, particularly GO-PS B and GO-PS C change similarly over time, showing no significant difference. In Fig.3(c), adding cement pore solution increases particle size for all GO-PS suspensions with a more pronounced impact on GO without PS. This aligns with the zeta potential results, where the high ionic strength neutralizes surface charges and causes agglomeration. However, GO-PS suspensions remain relatively stable due to steric hindrance provided by PS, which mitigates cation adsorption and prevents excessive agglomeration.

### 3.3 Characterization of the suspensions by visual imaging

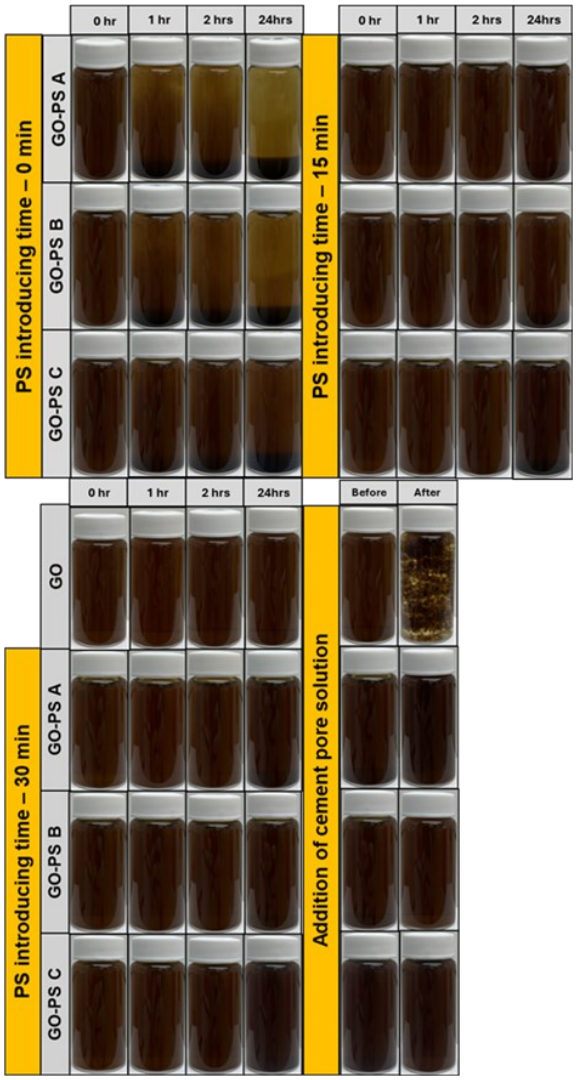


Fig.4 Sedimentation states of GO with and without PS

Fig.4 presents the naked-eye observation of sedimentation states of GO with and without PS. The images of the GO and GO-PS suspensions underscore the importance of the timing of PS addition during ultrasonication and the behaviour of the suspensions in cement pore solution. The timing of PS introduction during ultrasonication significantly affects the stability of the suspension. Sedimentation began as early as 1 hour when PS was introduced at 0 min, before the commencement of ultrasonication, and it progressed over time, indicating poor stabilization. Introducing PS after 15 minutes of the ultrasonication process appeared to enhance dispersion stability, as no noticeable sedimentation was observed within the first 24 hours. The best stability was observed when PS was introduced after 30 minutes of ultrasonication, with only negligible sedimentation reported even after 24 hours. These findings highlight that a delayed introduction of PS during ultrasonication optimizes its stabilizing effect, likely due to improved interaction and adsorption of PS onto the GO surface under optimal conditions.

In the GO suspension without PS, agglomeration began immediately upon the addition of cement pore solution. The agglomeration was highly pronounced, indicating poor dispersibility in the alkaline environment. Conversely, GO-PS suspensions exhibited stabilization and dispersing properties, as no significant agglomeration was observed upon the addition of cement pore solution. This demonstrates that the PS addition effectively mitigates the agglomeration of GO in cement pore solution.

### 3.4 Compressive strength of cement mortar incorporating GO

Finding the superplasticizer compatible with GO requires validation via mechanical tests [15]. The effect of GO with various types of PS on the compressive strength of cement mortar with a GO dosage of 0.02% was evaluated, as shown in Fig.5.The figure shows that compared to the control sample, the 7 days compressive strengths of cement mortar incorporating GO, GO-PS A, GO-PS B and GO-PS C were increased by 1.9%,1.7%,7.5%, and 8.2% respectively. This experimental result leads to the conclusion that incorporating dispersed GO can improve the mechanical strength of mortar.

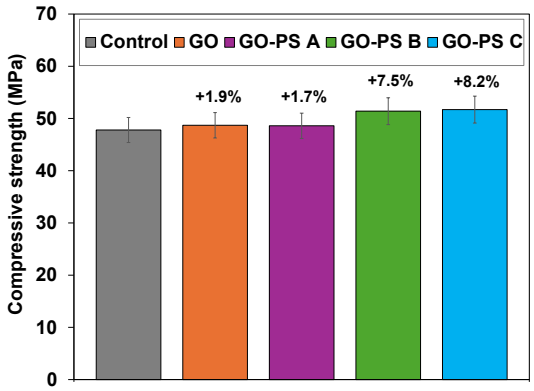


Fig.5 Compressive strength (7 days) of GO-added mortar with different PSs

## 4. CONCLUSIONS

This study investigated the dispersion of GO in cement mortar through different approaches of dispersion with a keen focus on superplasticizers introducing time during ultrasonication and the type of superplasticizers. The following highlights presents some of the key findings:

- The introduction of a superplasticizer after 30 minutes of ultrasonication improved the dispersion and stability of graphene oxide, allowing better exfoliation and surface interaction.
- Among the tested PSs, PS-C is the most effective, achieving the most negative zeta potential and the smallest particle size and superior stability in high ionic strength conditions.
- An appropriate superplasticizer is essential to achieve optimal performance in GO-added mortar. Properly dispersed GO with PS C resulted in an 8.2% increase in compressive strength at 7 days compared to other PSs.
- Optimum dispersion and stability of GO can be achieved through the right selection of superplasticizer and its proper time of introduction during ultrasonication, which will eventually lead to high-performance cementitious materials.

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