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Improving the early mechanical properties of a pozzolan-added cement-based material by adding Nano C–S–H

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The mechanical properties of the pozzolan-added cement material with the addition of nano C–S–H have been studied. A mechanism that influences on them is proposed. X-ray diffraction (XRD), scanning electron microscopy (SEM), and mercury intrusion porosimetry (MIP) were used to characterize the microstructure of the pozzolanic mortar. The results showed a significant effect of property improvement when using nano-sized C–S–H: the compressive strength increased from 22.3 MPa to 33.2 MPa after 7 days. SEM images showed that after the addition of nanosized C–S–H, the matrix became more compact and the number of defects decreased. X-ray analysis confirmed that the addition of nanosized C–S–H increased the amount of C–S–H formed during hydration. The MIP results showed that nanoscale CSH improves the pore structure of the mortar and significantly reduces the porosity. All microscopic measurements showed that nanosized C–S–H accelerates the process of cement hydration and forms more hydration products, which contributes to the modification of the interfacial transition zone of the solution and increases the compactness of the matrix. This is the main reason for improving the initial mechanical properties of the cement-based pozzolanic mixture.

Keywords: pozzolan, nanosized C–S–H, early mechanical properties, hydration acceleration.

Поліпшення вихідних механічних властивостей змішаного з пуцоланом цементного матеріалу за рахунок додавання Nano C–S–H. *Іхуей Чжун, Ган Ляо*

Вивчено механічні властивості цементного матеріалу, змішаного з пуцоланом, з добавкою нанорозмірного C–S–H. Запропоновано механізм впливу на них. Рентгенівська дифракція (XRD), скануюча електронна мікроскопія (SEM) та ртутна інтрузійна порометрія (MIP) були використані для характеристики мікроструктури пуцоланового розчину. Результати показали, що ефект поліпшення властивостей використання нанорозмірного C–S–H був значним: міцність на стиск збільшилася з 22,3 МПа до 33,2 МПа через 7 днів. СЕМ-зображення показали, що після додавання нанорозмірного C–S–H матриця стала компактнішою, а кількість дефектів зменшилася. Рентгенівський аналіз підтвердив, що додавання нанорозмірного C–S–H збільшує кількість C–S–H, що утворюється під час гідратації. Результати MIP показали, що нанорозмірний C–S–H покращує пористу структуру будівельного розчину та значно знижує пористість. Всі мікроскопічні вимірювання показали, що нанорозмірний C–S–H прискорює процес гідратації цементу та утворює більше продуктів гідратації, що сприяє модифікації міжфазної перехідної зони розчину та збільшення компактності матриці. Це є основною причиною покращення вихідних механічних властивостей пуцоланово суміші на цементній основі.

1. Introduction

With the rapid development of water conservancy and hydropower engineering construction in China, the demand for mineral admixtures in hydraulic concrete is increasing. Due to the tight supply of fly ash or slag in western China, there has been a necessary trend towards the local development of mineral additives with pozzolanic activity, partially or completely replacing fly ash in hydraulic concrete. This approach can not only eliminate the traditional shortage of mineral supplements, but also achieve the goal of energy saving and emission reduction [1–4].

Pozzolan is a mineral resource abundant in the western region of China, which contains a large amount of silicon and aluminum elements, as well as substantial amounts of amorphous glass that exhibits some pozzolanic activity. It can be used as a concrete mineral admixture to partially replace cement. Currently, researchers have conducted a significant amount of research on pozzolan as a mineral admixture. T?rkmeno?lu et al. [5] reported that petrographical analysis on pozzolan via optical microscopy, XRD, SEM-EDX, and spectroscopic techniques are effective in evaluating the suitability of pozzolan in pozzolanic cements. Messaouda et al. [6] explored the possibility of substituting sand with calcareous pozzolan in concrete production. Liguori et al. [7] demonstrated the feasibility of producing environmentally friendly binders using zeolitized pozzolan.

However, after adding pozzolan, the early strength of cement-based material was reduced. And some early strength agents were used to solve this issue [8]. In this paper, nano C–S–H was used to improve the early mechanical property of pozzolan added cement mortar. The content of pozzolan was fixed and different dosage of nano C–S–H was adopted. The microstructure of the mortar including phase composition and micromorphology of the hydration products were characterized, and the mechanism was analyzed. This work can significantly improve the early mechanical properties of pozzolan added concrete and may promote the application of pozzolan in hydraulic concrete.

2. Experimental

2.1 Materials

Cement used in this study was conch brand P·O 42.5, and pozzolan was purchased online. The chemical composition of cement and pozzolan are shown in Table 1. Pozzolan was sieved by a 300-mesh sieve and its particle size was close to that of cement. Nano C–S–H was purchased from China Changan Building Material Company. Nano C–S–H was a white suspension with solid content of 20 %, and the size of most particles was below 100 nm. ISO standard sand was used as fine aggregate.

2.2 Mix proportion

The composite cementitious material consisted of 80 % cement and 20 % pozzolan by mass fraction. The water-binder ratio was fixed as 0.45 and the binder-sand ratio was 0.33. Different amounts of nano C–S–H were added and the contents of nano C–S–H were 1.25 %, 2.5 % and 3.75 % by mass of cementitious material. The detailed mix proportions are shown in Table 2.

2.3 Sample fabrication

Firstly, raw materials were prepared according to the mix proportions outlined in Table 2. Cement, pozzolan and sand were mixed together in an agitator kettle. Then

Table 1. Chemical composition of cement and pozzolan (wt.%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	$Na_2O + K_2O$	LOI
Cement	41.53	25.92	11.96	5.52	6.43	5.07	1.15	2.42
Pozzolan	0.57	83.01	7.92	0.56	0.41	0.17	0.48	4.56

Table 2. Mix proportions

No.	Cement, g	Pozzolan, g	Sand, g	Water, g	Superplasticizer, g	Nano C–S–H, g
N0	500	/	1500	225	2.5	/
N1	400	100	1500	225	2.5	/
N2	400	100	1500	225	2.5	6.25
N3	400	100	1500	225	2.5	12.5
N4	400	100	1500	225	2.5	18.75

half of the required water was added to the solid mixture, and the mixture was stirred slowly for 30 seconds. Next, the rest portion of water and superplasticizer were added to the mixture, followed by a fast 30-second stirring process to improve workability. The nano C–S–H was added to the mixture and stirred for another one minute. Finally, the mixture was cast into molds with the size of 40×40×160 mm. Samples were fetched out from the molds after one day. After cured in a standard condition for 3 and 7 days, the samples were used to test the mechanical properties and determine the microstructure.

2.4 Characterization

According to the Chinese standard GB/T17671-1999, the compressive strength of all samples was tested. After the measuring mechanical properties, the broken samples were immersed into absolute ethyl alcohol to inhibit hydration. The phases of the samples were then determined using X-ray diffraction (XRD). The micromorphology of the mortar was subsequently observed via scanning electron microscopy (SEM). Finally, the pore structure of the mortar was analyzed using mercury intrusion porosimetry (MIP).

3. Results and discussion

3.1 Mechanical properties

Fig. 1 shows the compressive strength of samples at different ages. Comparing N0 and N1, it can be found that the early compressive strength of N1 was significantly reduced after adding pozzolan. This was mainly due to the replacement of cement with pozzolan. In particular, the activity of pozzolan was lower than that of cement clinker, resulting in lower alkalinity and slower hydration rates. However, after adding nano C–S–H, the compressive strength of samples (N2, N3, and N4) increased compared to N1. The compressive strength of each specimen increased with nano C–S–H content, but the rate of increase in strength decreased with curing age. In detail, the strength increase rate reached the maximum after 3 days, and the strength increase was the greatest after 7 days, which indicated that nano C–S–H mainly played a role in the early stage, especially in the first 3 days, and contributed little to long-term mechanical properties. In addition, sample N4 with nano C–S–H content of 3.75 % by mass of cementitious material had the highest compressive strength of 33.2 MPa after 7 days, which was 29.8 % higher than that of sample N1. Previous studies have shown that the hydration process of cement can be divided into several stages, including the induction period (first 4 h), acceleration period (4–12 h), and deceleration period (after 12 h). Obviously, the strengthening effect of nano C–S–H was more significant during the acceleration period than during the deceleration period. Therefore, it can be inferred that the addition of nano C–S–H mainly changed the hydration rate of pozzolan blended cement, which was related to the early compressive strength of pozzolan added cement-based materials. This can be explained from the strength theory of cement-based materials. An increase in the early strength of pozzolan added mortar was mainly attributed to the enhanced hydration degree of cementitious materials, which was induced by the accelerating effect of nano C–S–H. In particular, nano CSH was adsorbed on cement and pozzolan particles, and acted as a nucleation site, reducing the nucleation barrier of the cement hydration system and promoting the formation of C–S–H gel. As a result, the content of hydration products was improved and the early compressive strength was enhanced.

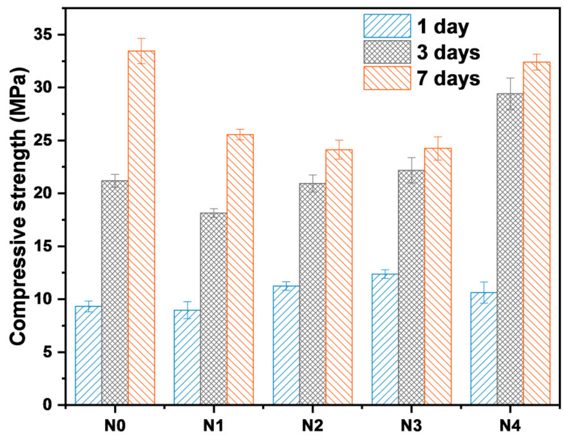

Fig. 1. Early compressive strength of samples at different curing ages.

3.2 XRD analysis

Fig. 2 presents the X-ray diffraction patterns of different samples after 7 days of curing. It can be seen that the addition of nano C–S–H had little effect on the composition of the crystalline phase of the pozzolan added mortar, which mainly consisted of cement hydration products and aggregates. Among them, $Ca(OH)_2$ was the main hydration product, and its diffraction peak intensity increased with an increase in the nano

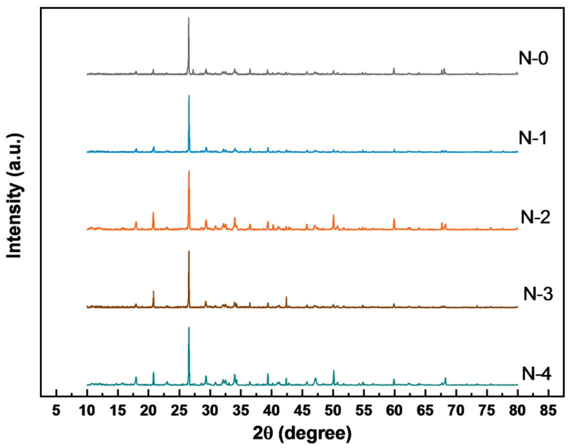

Fig. 2. X-ray diffraction patterns of samples after 7 days of curing.

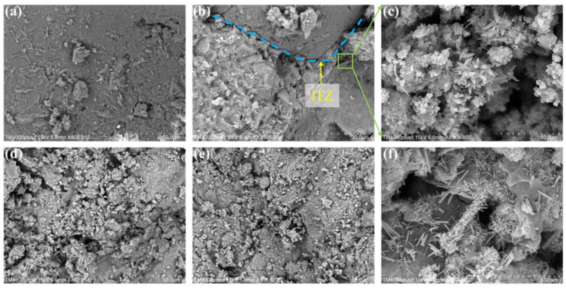

Fig. 3. SEM images of samples after 7 days of curing: (a) N0, (b) N1(×1500), (c) N1(×4000), (d) N2, (e) N4(×800), (f) N4 (×7000).

C–S–H content, confirming its strong promotion effect on cement hydration. However, no diffraction peaks of nano C–S–H was observed, probably because the content of nano C–S–H was low and the C–S–H formed during the hydration process was amorphous, resulting in no characteristic diffraction peaks. It should be noted that the relative diffraction intensity of $Ca(OH)_2$ varied with nano C–S–H content, and tended to be stable after 7 days of hydration, indicating that nano C–S–H was more likely to affect the hydration degree of cement slurry in the early stage of hydration; this is consistent with the results of early compressive strength. In addition, the diffraction intensity of quartz was particularly significant, which was attributed to the presence of quartzs and and was unrelated to the hydration reaction. These results were of great significance for optimizing the composition and properties of pozzolan containing mortar.

3.3 SEM images

As shown in Fig. 3(a), the matrix of N0 sample was compacted after 7 days of curing. It can be seen that lamellar hydration products were wrapped with C–S–H gel; there were almost no micro-cracks, which suggested that the hydration of cement was sufficient. After adding pozzolan, as the hydration degree of cement was reduced, the micro-structure of cement was also changed. Fig. 3(b) shows that the microstructure of the N1 sample with addition of pozzolan was loose with a large number of voids, which was the main reason for its low strength. In addition, the interfacial transition zone (ITZ) between the cement paste and aggregate was remarkable as the blue line indicated. In Fig. 3(c), micro-cracks, large holes, and hydration products with large size can be observed. Due to the high water-absorption capacity of pozzolan, a large number of water molecules were adsorbed on its surface, resulting in a high local water-to-cement ratio, which can easily generate more voids and oriented crystal growth at the interface. Therefore, ITZ was the weakest part in the whole cement matrix. Under loading, the aggregate and hydration products were most prone to crack along ITZ, which manifested a low strength grade at the macroscopic level. As mentioned before, the hydration process of the cement paste was significantly accelerated with addition of nano C–S–H. Fig. 3(d) and Fig. 3(e) showed that the cement matrix of N2 and N4 samples were more compacted than that of N1. With an increase in the nano C–S–H dosage, more hydration products were generated. As shown in Fig. 3(f), numerous small needle-/rod-shaped ettringite and flocculent C–S–H gel were formed locally, which was the main contributor to the early strength of samples, and these hydration products were uniformly distributed. Due to the pozzolanic effect, the amount of large-sized hydration products was reduced, and weak ITZ properties have been @improved, resulting in a significant increase in early strength.

3.4 MIP analysis

Fig. 4 shows the pore size distribution curves based on the pore volume of the samples. Pore size distribution curves presented bimodal distribution and pore diameter of all samples ranged from 10 nm to 1 μm. Before adding pozzolan, the most probable pore diameter of N0 sample was about 20 nm, and the total porosity was 7.2109 %, and the pores smaller than 100 nm accounted for 99.36 %. After add-

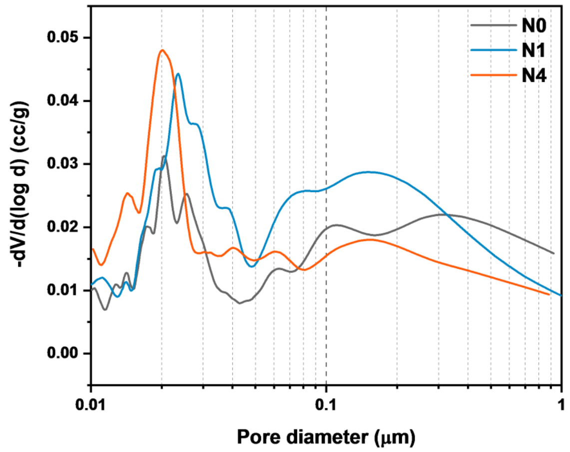

Fig. 4. Pore diameter distribution curves of samples.

ing pozzolan, due to the decreased hydration rate, the most probable pore diameter was about 25 nm for N1 sample, and the pores smaller than 100 nm accounted for 99.27 %. In addition, the fractal dimension of N1 (2.6784) was lower that of N0 (2.7314), indicating that more gel pores were formed in N0 due to the higher hydration degree. It should be noted that the total porosity of N1 was lower than that of N0 shown in Table 3. This can be explained by the fact that the pozzolan was finer than the cement particles, and these unreacted pozzolan particles had a good filling effect, thereby reducing the porosity. After introducing nano C–S–H, the total porosity of N4 significantly decreased to 5.2515 %, the pore content (d nm) increased to 99.66 %, and the fractal dimension was 3.2281. This shows that the pore diameter has been further reduced and the microstructure has also improved, which is mainly due to two factors: the accelerating effect of the nano C–S–H and the filling effect of pozzolan.

3.5 Mechanism

C–S–H, as one of the primary hydration products of cement, had similar morphology, particle size, and crystal structure with the nano-sized C–S–H utilized in this study. During the hydration process of cement, the nano-sized C–S–H can serve as nucleation sites by reducing the heterogeneous nucleation barrier of C–S–H. As a result, the hydration rate of cement was accelerated and more hydration products were generated, thus improving pore structure and interfacial transition zone and reducing the number of microscopic defects. In addition, the pozzolanic effect can further optimize the microstructure of the cement matrix. The filling effect of pozzolan was also significant, resulting in a more compacted matrix. Therefore, due to aforementioned mechanisms, the mechanical performance of the cementitious matrix can be significantly improved.

Table 3. Pore structure parameters of samples

No.	Porosity	Pore diameter distribution (number)		Fractal dimension
		<100 nm	>100 nm	
N0	7.2109 %	99.36 %	0.64 %	2.7314
N1	6.7354 %	99.27 %	0.73 %	2.6784
N4	5.2515 %	99.66 %	0.34 %	3.2281

4. Conclusions

Due to the low reactivity of pozzolan, after being added into cement-based materials, the pH of the cement system will be reduced, resulting in a decrease in the hydration rate and hydration products, thus causing a decline in early mechanical properties. The effect of nano-sized C–S–H on improving the early strength of mortar was significant. When the mass fraction of nano-sized C–S–H was 3.75 %, the 7-day strength of the sample was the highest, and the compressive strength reached 33.2 MPa. XRD results showed that after introducing nano-sized C–S–H, the phase composition of hydration products did not change, but the quantity of hydration products increased, especially C–S–H. SEM images showed that nano-sized C–S–H significantly reduced the number of large pores in the matrix, which played a crucial role in improving the early compactness of mortar and improving the interfacial transition zone. MIP results showed that after adding nano-sized C–S–H, the porosity of mortar decreased with an increase in the nano-sized C–S–H content. The pore structure became more refined and complex due to the accelerating effect of nano-sized C–S–H. In summary, nano-sized C–S–H can promote the hydration process of cement, improve the microstructure of pozzolan added mortar, and enhance the early mechanical properties, thus improving @the production efficiency.

References

1. B.Yilmaz, A.Ucar, B.Oteyaka et al., *Building and Environment*, **42**, 3808 (2007).

2. S.Liu, P.Fang, H.Wang et al., *Powder Technology*, **380**, 59 (2021).
3. M.Meziani, N.Leklou, N.Chelouah et al., *Construction and Building Materials*, **318**, 126008 (2022).
4. B.Liguori, F.Iucolano, B.de Gennaro et al., *Construction and Building Materials*, **99**, 272 (2015).
5. A.G.Turkmenoglu, A.Tankut, *Cement and Concrete Research*, **32**, 629 (2002).
6. M.Cherrak, A.Bali, K.Silhadi, *Construction and Building Materials*, **47**, 318 (2013).
7. B.Liguori, F.Iucolano, B.de Gennaro et al., *Construction and Building Materials*, **99**, 272 (2015).
8. W.He, G.Liao, *Functional Materials*, **28**, 737 (2021).