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Influence of nano-C–S–H on the mechanical properties of recycled concrete

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In this paper, in order to improve the mechanical property of recycled concrete, nano-C–S–H was added to modify recycled concrete, and the mechanism of the improvement was also discussed. The methods of X-ray diffraction (XRD), Scanning electronic microscope (SEM), and Mercury intrusion porosimetry (MIP) were applied to characterize the microstructure of nano-C–S–H modified recycled concrete. The results showed that the effect of nano-C–S–H was remarkable, namely, the 7-day compressive strength increased from 22.5 MPa to 33.5 MPa and flexural strength from 1.74 MPa to 2.25 MPa. SEM images showed that the matrix of recycled concrete became denser after adding nano-C–S–H. XRD confirmed that the hydration product increased with the addition of nano-C–S–H. MIP results demonstrated that the pore structure was refined by nano-C–S–H and porosity of recycled concrete was reduced noticeably. All measurements proved that the hydration process of cement was accelerated by nano-C–S–H and more hydration products had been produced, which contributed to densify the microstructure of recycled mortar and was the main reason for improving the mechanical properties of recycled mortar.

Keywords: recycled concrete, recycled cement powder, nano-C–S–H, improved mechanical properties.

Вивчення впливу нано-C–S–H на механічні властивості вторинного бетону. *Wei He, Gang Liao.*

Досліджено вплив нано-C–S–H на механічні властивості вторинного бетону. Дослідження проведено методами дифракції рентгенівських променів (XRD), скануючої електронної мікроскопії (SEM) та порозиметрії проникнення ртуті (MIP). Результати показали, що ефект нано-C–S–H є значним, а саме, 7-денна міцність на стиск вторинного бетону збільшилася з 22,5 МПа до 33,5 МПа, міцність на згин збільшилася з 1,74 МПа до 2,25 МПа. SEM зображення показали, що після додавання нано-C–S–H матриця вторинного бетону стала щільнішою. XRD підтвердив, що вміст гідратації продукту збільшувався при додаванні нано-C–S–H. Результатами МІП доведено, що пориста структура покращувалася завдяки додаванню нано-C–S–H, пористість вторинного бетону помітно зменшилася. Усі виміри свідчать, що процес гідратації цементу був прискорено за рахунок нано-C–S–H, вихід продуктів гідратації збільшувався, що сприяло ущільненню мікроструктури вторинного бетону та є основною причиною покращення механічних властивостей вторинного бетону.

Исследовано влияние нано-C–S–H на механические свойства рециклированного бетона. Исследования проведены методами дифракции рентгеновских лучей (XRD), сканирующей электронной микроскопии (SEM) и порозиметрии проникновения ртути (MIP). Результаты показали, что эффект нано-C–S–H изначительный, а именно, 7-дневная прочность на сжатие вторичного бетона увеличилась с 22,5 МПа до 33,5 МПа, прочность на изгиб увеличилась с 1,74 МПа до 2,25 МПа. SEM изображения показали, что после добавления нано-C–S–H матрица вторичного бетона стала более плотной. XRD подтвердил, что содержание продукта гидратации увеличивалась при добавлении нано-C–S–H. Результаты MIP свидетельствуют, что пористая структура улучшается благодаря добавлению нано-C–S–H, при этом пористость вторичного бетона заметно уменьшается. Все результаты исследования свидетельствуют, что процесс гидратации цемента ускоряется за счет нано-C–S–H. Выход продуктов гидратации увеличивается, что способствовало уплотнению микроструктуры вторичного бетона и является основной причиной улучшения механических свойств вторичного бетона.

1. Introduction

Recycled Concrete Powder (RCP) is a by-product and the accumulation of RCP will lead to many environmental problems such as water polution and land pollution. On the other hand, the chemical composition of RCP is similar to that of cement, and RCP exhibits some potential hydration activity [1-4]. Therefore, using RCP to produce recycled concrete is a viable way to process RCP. Previous research has shown that RCP can be used as an additional binder and replace a certain proportion of cement. Nevertheless, the greatest disadvantage is that the activity of RCP is relatively low, so the mechanical property of recycled concrete is poor, which limits its application and utilization. In general, the poor mechanical properties are due to two main factors [5,6]. Firstly, RCP has a high adsorption capacity to water, which leads to poor workability of the recycled concrete. In actual use, a superplasticizer can be added to improve flow, but the setting process of the recycled concrete will be delayed by the superplasticizer. Secondly, the RPC activity is low, so the initial compressive strength of the recycled concrete is too low to guarantee performance. Researchers proposed many solutions to improve the initial compressive strength of recycled concrete, but improvement effect was not noticeable.

Recently, nanotechnology has shown great promise in improving the mechanical properties of cement-based materials. A variety of nano-materials have been used to enhance the compressive strength of cement-based materials, such as carbon nanotubes (CNT), nano-SiO_2, and nano-hydrated calcium silicate (C–S–H) [7,8]. The mechanisms of the improvement effect caused by nanotechnology differ depending on the nanomaterials. For example, CNTs can act as nano-fibers that inhibit the development of microcracks and reduce microdefects. Nano-SiO_2 is not saturated with silicon-oxygen tetrahedra and has high activity, which allows it to react with alkaline substances in the cement hydration medium and accelerate the hydration process. It should be noted that C–S–H is one of the cement hydration products. Some researchers have found that even a small addition of nano-C–S–H to cement can significantly improve the initial compressive strength of concrete [9]. This reinforcing effect is believed to be related to the nano-C–S–H's ability to nucleate, which aids cement hydration. However, only a few studies have been published on enhancing the strength of recycled concrete with nano-C–S–H. In this study, the aim is to improve the mechanical property of recycled concrete by incorporating nano-C–S–H and reveal the mechanism of this enhancement effect. In theory, nano-C–S–H can accelerate the hydration of cement and improve the strength of concrete, and this enhanced strength can compensate the strength loss caused by RCP [10-12]. The amount of nano-C–S–H is a key factor affecting the mechanical property, which has been studied in detail. Several advanced methods were used to characterize the microstructure of the nano-C–S–H added system. This work may provide a new method to enhance the mechanical property of recycled concrete and promote its application.

2. Experimental

2.1 Raw materials

Cement used in this study was grade P·O 42.5, and all properties were in accordance with the Chinese standard GB175-2007. RCP was obtained from an aggregate processing plant and sieved through a 100-mesh screen, and the chemical composition of RCP is shown in Table 1. Nano-C–S–H was a commercial product provided by China Changan Building Material Company. Nano-CSH was a white suspension with a solids

Table 1. Chemical composition of RCP (wt %)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O
31.03	47.49	11.71	2.96	2.04	0.91	1.85	1.08

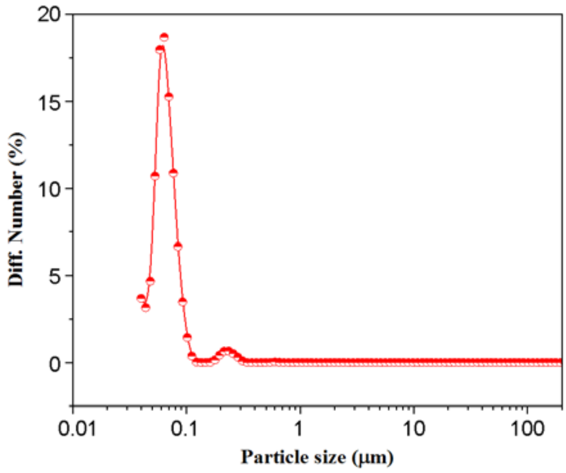

Fig. 1. Particle size distribution of nano-C–S–H.

content of 20 %, and most of the particles were less than 100 nm in size, as shown in Fig. 1, indicating that the CSH was at nanoscale and the average particle size was about 70 nm.

2.2 Design of mix proportion

The water to cement ratio was fixed at 0.36 and the cement to sand ratio was fixed at 0.33. The weight fraction of RCP was 15 %. To investigate the effect of nano-C–S–H content on mechanical properties, various amounts of nano-C–S–H were added. And the content of nano-C–S–H ranged from 0.25 % to 0.75 % by mass of cementitious material. The detailed mix proportions are shown in Table 2.

2.3 Sample preparation

Firstly, a certain amount of raw materials were prepared as indicated in Table 2. Cementitious materials and sand were mixed in a kettle with a stirrer, and then half of the water was added to the solid mixture. Secondly, the mixture was slowly stirred for 30 s, and subsequently another part of water and superplasticizer were added to the mixture, followed by rapid mixing for 30 s to obtain excellent workability. Thirdly, nano-C–S–H was added into the mixture and stirred for 60 s. Finally, the mixtures were molded (40×40×160 mm^3) and the samples were demolded after one day and cured in a standard room for 3 days and 7 days.

2.4 Characterization

The flexural strength and compressive strength of all samples was measured according to Chinese standard GB/T17671-1999. After measurement of the mechanical properties, the broken samples were immersed in absolute ethanol to prevent future hydration. X-ray diffraction (XRD) was used to measure the phase composition of samples. Scanning electronic microscope (SEM) was applied to observe the micromorphology of concrete. Mercury intrusion porosimetry (MIP) was used to analyze the pore structure of concrete.

3. Results and discussion

3.1 Mechanical property

Fig. 2a and 2b present the compressive and flexural strength of samples, respectively. After incorporating RCP, it can be found that the compressive and flexural strength of G1 was slightly increased compared to G0. This was because the particle size of the recycled powder was close to that of the cement, which played the role of a filler at the early stage and can compact the pore structure of the cement paste; the RCP had a certain hydration activity, which can react with the cementitious material to improve its early strength. However, due to the strength hysteresis effect of the superplasticizer, the early strength of G0 and G1 samples were still low. The strength of all samples increased with the content of nano-C–S–H, but the strength increasing rate decreased over time. Specifically, the strength increasing rate at 3 days was the highest, and the strength at 7 days was the highest, which indicated that nano-C–S–H mainly worked in early stages especially the first 3 days and contributed little to long-term strength. Moreover, the compressive

Table 2. Mix proportion

No.	Cement, g	RCP, g	Sand, g	Water, g	Superplasticizer, g	Nano-C–S–H, g
G0	450	/	1350	162	2.7	–
G1	382.5	67.5	1350	162	2.7	–
G2	382.5	67.5	1350	162	2.7	5.625
G3	382.5	67.5	1350	162	2.7	11.25
G4	382.5	67.5	1350	162	2.7	16.875

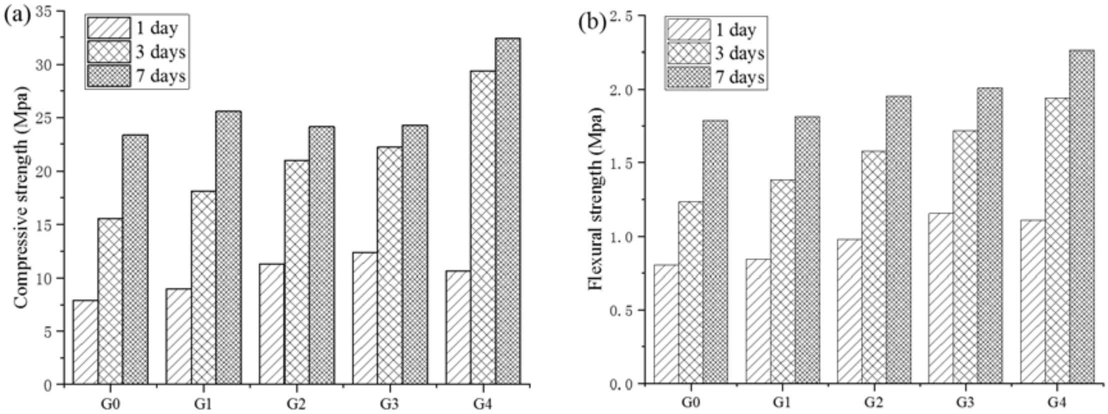

Fig. 2. (a) Compressive strength of samples; (b) flexural strength of samples.

strength of sample G4 with 3.75 % of nano-C–S–H (based on the quality of cementitious materials) was the highest at 7 days, reaching 33.5 MPa, which was 44 % higher than that of sample G0; and the 7-day flexural strength was also increased by about 28.5 %. Other studies have shown that the cement hydration process can be divided into several stages: an induction period (first 4 h), an accelerating period (4–12 h), and a deceleration period (after 12 h). It's interesting that the enhancing effect of nano-C–S–H was more obvious in the accelerating period than in the deceleration period. Therefore, it can be inferred that the enhanced strength of recycled concrete caused by the addition of nano-C–S–H was associated with the cement hydration rate. According to the hydration-strength theory of cement-based materials, the improvement of early strength of recycled concrete by nanotechnology reinforcement was mainly attributed to the promotion of early cement hydration by nano-C–S–H and an increase in the hydration degree. Specifically, C–S–H nano-particles worked as nucleation centers, and nanocrystalline nuclei reduced the nucleation barrier of the cement hydration system, promoting the formation of C–S–H gel and improving the early strength. The detailed mechanism would be confirmed by the following analysis.

3.2 Phase composition

Fig. 3 shows X-ray diffraction patterns of various recycled concrete. It can be seen that the amount of nano-C–S–H had little effect on the crystal phases of recycled concrete. The phase composition can be devided of two categories: hydration products and aggregates. The main hydration product was $Ca(OH)_2$, and its diffraction peak intensity increased with increasing nano-C–S–H content, confirming the intense effect of promoting hydration with nano-C–S–H. However, diffraction peaks of nano-C–S–H were not observed; this may be attributed to the fact that the content of the added nano-C–S–H was small, and the C–S–H formed during the hydration process was amorphous. It should be also noticed that the relative diffraction intensity of $Ca(OH)_2$ changes with nano-CSH content and finally becomes stable after 7 days of hydration, which demonstrates that the degree of hydration of cement pastes is easily influenced by nano-CSH in the early hydration stage. The diffraction intensity of quartz was high, which was caused by the sands and had little to do with the hydration reaction.

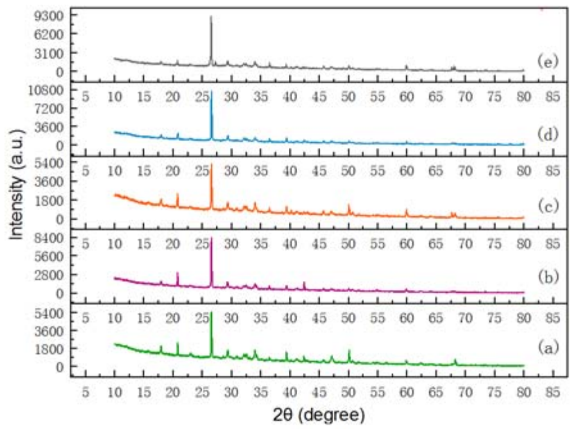

Fig. 3. X-ray patterns of (a) G0-7, (b) G1-7, (c) G2-7, (d) G3-7, and (e) G4-7.

3.3 Micromorphology

Fig. 4 shows the microstructure of the samples. As shown in Fig. 4a, after seven days of hydration, the microstructure of the sample G0 without RCP was loose and there

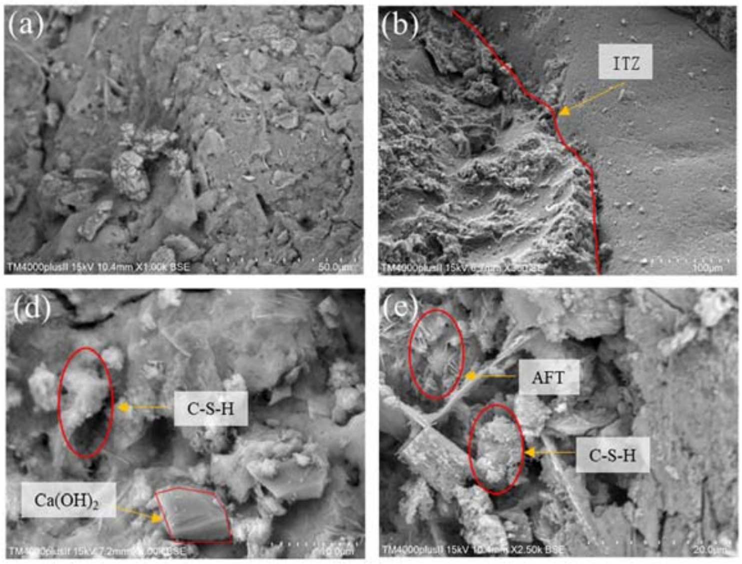

Fig. 4. SEM images of (a) G0-7, (b) G1-7, (c) G2-7, (d) G3-7, and (e) G4-7.

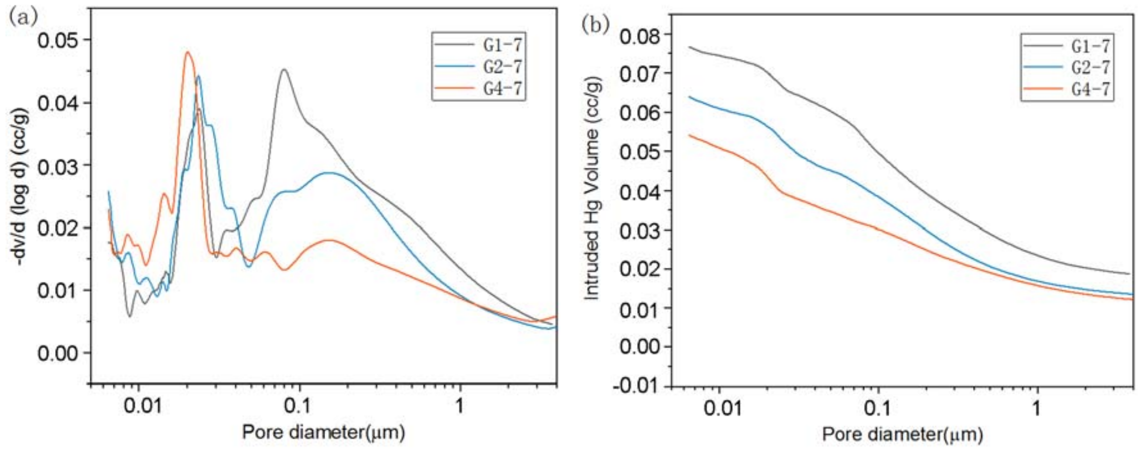

Fig. 5. (a) Pore size distribution curves; (b) cumulative distribution curves.

were many holes, which was the main reason for the low strength. As shown in Fig. 4b, the microstructure of hardened cement paste was improved after the incorporation of recycled powder. The compatibility between RCP and fresh cement paste was good, and there was no obvious stratification. G1 was denser than G0, and a small amount of C–S–H gel could be observed. However, the interfacial transition zone (ITZ) between cement paste and aggregate was still observed. Due to the high water absorption rate of RCP, a large number of water molecules were adsorbed on its surface, which led to a high local water-cement ratio resulting in more voids at the interface and oriented crystal growth. Consequently, ITZ was the weakest part of the entire matrix, stress easily led to cracking, and the strength was low. After adding the nano-C–S–H, the hydration process of the cement paste was obviously accelerated, as shown in Fig. 4c; a large amount of acicular ettringite was produced in situ, which was a major contributor to the early strength of the sample G-2. With an increase in the amount of nano-C–S–H, more hydration products appeared, and the ITZ was improved. As shown in Fig. 4(d), hexagonal lamellar $Ca(OH)_2$ and a large amount of amorphous C–S–H gels were observed, and the amount of ettringite was significantly reduced. G-4 sample had the same characteristics as G-3 sample, but G-4 sample was denser and had more C–S–H gels as shown in Fig. 4e.

3.4 Pore structure

Fig. 5 shows the pore size distribution curves of different recycled concrete. As seen in Fig. 5(a), the curve of G1-7 showed a bimodal pore size distribution at 80 and

25 nm, and most probable pore size was 80 nm. Samples G2-7 and G4-7 also showed a bimodal distribution, but location and value of the two peaks were totally different from that of G1-7; that is, the most probable pore size of G2-7 and G4-7 were 25 and 20 nm, respectively. It can be seen that pore size of recycled concrete shifted to smaller values after adding nano-C–S–H; the pore size diameter decreased with the nano-C–S–H content, indicating that after adding nano-C–S–H, the hydration reaction was accelerated and the pores the pores were filled with hydration products. After 7 days of hydration, the most probable pore sizes of all samples became smaller, and the pore size distribution curves presented complex multimodal distribution. As shown in Fig. 5b, the cumulative pore size distribution curve of G4-7 was obviously lower than that of G1-7 and G2-7, while the porosity decreased from 7.5 % to 5.5 %. After 7 days of hydration, the porosity of all samples decreased to about 5 %, indicating that the compaction effect caused by nano-C–S–H was evident within 7 days and this effect was enhanced with content of nano-C–S–H.

3.5. Mechanism

First, nano-sized particles of C–S–H were used in this study, which can be nucleation centers in the hydration of cementitious materials. In addition, C–S–H is one of the main hydration products of cement, and the added C–S–H was similar to the formed C–S–H in morphology and crystal phase. Upon adding nano-C–S–H, the nucleation barrier of C–S–H on the heterogeneous interface noticeably decreases. The consequence is that more hydration products are produced in the same time, and these products are evenly distributed in the cement matrix, thus improving the pore structure of cement-based materials and reducing the number of defects. In macroscopic scale, the hydration rate of cement is accelerated and the corresponding mechanical property is obviously improved.

4. Conclusions

The recycled concrete powder has good compatibility with cement paste and certain hydration activity. Adding RCP, the microstructure of recycled concrete was denser, but the strength was low. The effect of nano-C–S–H on improving the early strength of recycled concrete was evident. The sample with addition of 3.75 % nano-C–S–H by mass of cementitious material had the highest 7-day strength, with compressive strength reaching 33.5 MPa and flexural strength reaching 2.25 MPa. SEM images showed that nano-C–S–H had a significant effect on improving the early densification degree of recycled concrete, greatly reducing the number of large pores in the paste. MIP results indicated that the porosity of recycled concrete was reduced after adding nano-C–S–H and decreased with nano-C–S–H content, and the pore structure was also compacted by the accelerating effect of nano-C–S–H. XRD results showed that the phase composition was not changed after introducing nano-C–S–H, but the amount of hydration product increased with the content of nano-C–S–H. It can be concluded that nano-C–S–H can facilitate the process of cement hydration and improve the microstructure of recycled concrete and give it increased strength, which can compensate for the loss of strength caused by the introduction of RCP.

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