An Insight into the Effect of Rice Straw Biochar on Compressive Strength and Thermal Conductivity of Cement

Dongyun Zhang¹, Tong Han², Jie Wang², Chengwan Sun², Xiao-yu Jiang², Zhenyu Ni² and Jianhua Guo²∗

¹ Geography Department, Handan College, Hebei, China
² College of Water Resources and Hydropower, Hebei University of Engineering, Handan 056107, Hebei, China
Email: *deny_gih@163.com.

Abstract: It is well known that it is very important to improve the quality of cement material concerning its compressive strength and thermal conductivity, which may reduce its quantity of usage and improve the heat maintenance of a structure compared with the traditional cement. In order to improve the properties of cement and other building materials, the test pieces were prepared by incorporating rice straw biochar with different pyrolysis temperatures into cement paste, and the compressive strength and thermal conductivity were tested after curing under both wet and dry conditions. The results showed that with the increase of biochar incorporation, the strength and thermal conductivity of the test blocks were decreased, but the thermal insulation performance of them was increased, and the quality and density of the test block were reduced. Under the condition of wet curing, the strength of the test pieces enhanced greatly with the dosage of 1% and 5%. When the dosage was 1%, the strength of the wet curing test block was the highest, which was increased by 51.06% compared with the blank control. The block strength increased by 14.98%; the thermal conductivity of the test piece incorporating biochar was reduced, and the test piece with 10% of the dry curing showed better thermal insulation performance, and the thermal conductivity was reduced by 39.21%. It can be seen that the addition of biochar improves the strength of the test block and optimizes the thermal insulation performance of the cement.

Keywords. Biochar; cement; compressive strength; thermal conductivity.

1. Introduction
Cement as anhydrous gel material is widely used in various construction fields and is still an irreplaceable product. In recent years, with the development of economy and industry, various kinds of large buildings, ultra-high type buildings, green buildings, ultra-light buildings, large span buildings and other special structures in the construction industry have been appearing, the performance of ordinary cementitious materials has been increasingly unable to meet our special requirements. Therefore, to provide an economical, green and better performance cementitious material has become more and more necessary for the development of the construction industry. Cement production as a silica raw material clay and coal consumption as fuel are very large, each production of 1 ton of cement clinker consumes about 0.16 tons of clay and 0.11 tons of standard coal, according to this calculation, China’s annual consumption of clay more than 100 million tons, the consumption of standard coal more than 80 million tons. At the same time, China is also a large agricultural country, rice straw as crop waste is particularly rich, accounting for 25% of China’s straw resources [1]. The pyrolysis of biomass such as straw under
fully or partially anoxic and anaerobic conditions produces a solid material rich in carbon and highly aromatized, which is called biochar [2]. Biochar consists of a carbon skeleton, which is chemically stable, and its porous structure makes it water-retentive, while it is a low thermal conductive and non-flammable material. It is also found that the amorphous silicon in rice straw gradually changes to the crystalline state after high temperature pyrolysis. These properties have great potential to improve the strength, thermal insulation and durability of the cementitious materials with biochar. Moreover, the preparation of biochar also provides a mechanism for the sequestration of atmospheric CO₂ [3]. Cement-based materials made from rice straw biochar also have the ability to capture atmospheric CO₂, a major greenhouse gas [4]. This reduces the emission of CO₂ in the atmosphere. These advantages indicate that rice straw biochar has great potential for modifying cement-based materials [1].

Strength and thermal conductivity, as the most important indexes of cementitious materials, have been the focus of research by many experts and scholars. Many foreign scholars have shown that the addition of biochar can enhance the mechanical properties and durability performance of cementitious materials. Biochar was added to the cementitious as an internal curing agent, and it was found that prepared biochar was more efficient in internal curing on the mortar and improved the strength and durability performance of the cement mortar [5, 6]. Biochar produced from sugarcane bagasse by low-temperature cracking was used to modify cementitious materials, and it was found that the addition of biochar significantly optimized the hydration properties and reduced the thermal conductivity of the cement slurry [7]. Wood waste biochar was incorporated into the cement base as a green admixture, and it was found that the incorporation of biochar slightly enhanced the cement hydration reaction and fixed the harmful substances in the cement [8]. A small amount of biochar rice husk ash was incorporated into concrete and it was found that the addition of rice husk ash could significantly enhance the hydration rate and compactness of concrete [9]. Moreover, the addition of a small amount of biochar can improve its physical properties. The effect of biochar burned from agricultural waste rice husk and sugarcane bagasse on the mechanical properties of concrete was investigated [10]. It was found that the compressive and tensile strengths of samples added with biochar were increased to different degrees. And the cement hydrates improved bonding strength and the carbonates densified microstructure can enhance the mechanical strength and carbon sequestration [11].

Finally, it was concluded that rice husk and sugarcane bagasse biochar can be reused in concrete without adverse environmental effects. In addition, studies have shown that using biochar to replace cement can reduce greenhouse gas emissions in the construction industry [4, 6, 12, 13].

Although scholars at home and abroad have studied the effects of various kinds of biochar on the properties of cementitious materials, there are still relatively few studies on rice straw biochar; moreover, there is no detailed study on the effects of rice straw biochar on ordinary silicate cement at different cracking temperatures and different admixtures; in addition, the test blocks are maintained only by standard maintenance, without simulating the sprinkling maintenance in actual engineering; therefore, this test Therefore, this test was conducted to test the strength and thermal conductivity of biochar by combining it with cement net paste at different admixtures, and to investigate the effects of pyrolysis temperature of biochar and test block maintenance conditions on strength and thermal conductivity.

2. Material Preparation and Testing

2.1. Biochar Preparation and its Characteristics
The raw material of biomass is Anhui rice straw, produced according to articles [14, 15], which is crushed by a grinder and placed in a crucible, and pyrolyzed using an intelligent temperature-controlled muffle furnace with a heating rate of 15°C/min, and then pyrolyzed for 4 hours after heating to the specified temperature to prepare rice straw biochar with six pyrolysis temperatures from 200°C to 700°C, and then removed after it cools naturally to room temperature. The prepared biochar pellets were ground by F-P2000E all-round planetary ball mill and passed through 100 mesh sieve, sealed in a dry and light-proof bottle and stored for use. The blank control and six different pyrolysis temperatures of rice straw biochar were indicated as CK, RS200, RS300, RS400, RS500, RS600 and RS700, respectively.
Calculation of biochar yields at different pyrolysis temperatures based on straw mass before preparation (M0) and biochar mass after preparation (M).

**Table 1.** Biochar yield and ash at different pyrolysis temperatures.

| Sample | RS200 | RS300 | RS400 | RS500 | RS600 | RS700 |
|--------|-------|-------|-------|-------|-------|-------|
| Productivity % | 61.04 | 42.48 | 38.23 | 33.98 | 33.57 | 31.19 |
| Ash content % | 77.67 | 46.92 | 39.34 | 36.01 | 34.89 | 34.17 |

**Table 2.** Quantitative analysis of biochar elements.

| Element | C | O | Ca | Si | Zr | K | Al | S | Na |
|---------|---|---|----|----|----|---|----|---|----|
| Weight % | 55.67 | 22.22 | 9.00 | 4.92 | 2.35 | 2.22 | 1.41 | 0.57 | 0.55 |
| Atoms % | 69.81 | 20.92 | 3.38 | 2.64 | 0.39 | 0.86 | 0.79 | 0.53 | 0.36 |

2.2. **Biochar Cement Test Block Preparation**

2.2.1. Cement. The cement was P.S.A 32.5R slag silicate cement from Handan GTC Taixing Cement Co. The density of cement is 2.8 g/cm³. The chemical composition of cement is shown in the following table.

**Table 3.** Cement chemical composition table.

| Composition | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | R₂O | Cl⁻ |
|-------------|------|-------|-------|-----|-----|-----|-----|-----|
| Content (wt%) | 26.48 | 10.09 | 2.58 | 51.81 | 3.96 | 2.54 | 0.57 | 0.04 |

2.2.2. Test Block Preparation. The biochar was substituted with 1%, 5% and 10% of the cement mass respectively. In order to make the cement and biochar mix evenly, the biochar and cement were firstly mixed fully until the mixture color was uniform before adding the quantitative tap water to mix the slurry fully and evenly, and poured into 70.7mm×70.7mm×70.7mm cement mortar molds, and the molds were manually vibrated until no bubbles were produced on the surface of the biochar cement slurry, and the molds were demolded after 24 hours. The test blocks were divided into two groups, one group was placed in the laboratory under dry environment for maintenance (temperature 25℃), and the other group was placed in water for standard maintenance (temperature 20℃±2℃), while maintained for 28 days. The labeling of each test block was indicated by the biochar number respectively.

**Table 4.** Table of different alternative ratio materials.

| Substitution ratio | Amount of cement/g | Carbon incorporation amount/g | Water volume/g | Water to ash ratio |
|-------------------|--------------------|-------------------------------|----------------|-------------------|
| 0%                | 1000.00            | 0.00                          | 430.00         | 0.43              |
| 1%                | 1000.00            | 10.10                         | 430.00         | 0.43              |
| 5%                | 1000.00            | 52.63                         | 520.00         | 0.52              |
| 10%               | 1000.00            | 111.11                        | 590.00         | 0.59              |

2.2.3. Test Block Density. According to Archimedes’ principle, the density of test blocks was calculated using the drainage method. Since the specific surface area of biochar particles is large, the density of cement test blocks will decrease as the amount of biochar increases. There is no significant difference in the density of cement test blocks mixed with biochar of different pyrolysis temperatures at the same substitution ratio, and the density of cement test blocks at different substitution ratios is given in the following table.
Table 5. Density of different alternative specific biochar cement blocks.

| Substitution ratio/% | 0   | 1   | 5   | 10  |
|----------------------|-----|-----|-----|-----|
| Density/(g/cm³)      | 1.88| 1.84| 1.78| 1.70|

2.3. Experimental Content

2.3.1 Compressive Strength Test. The test equipment used in the compressive strength test of sludge biochar cement test blocks was TAW-2000 microcomputer-controlled electro-hydraulic servo rock three-axis testing machine. Before conducting the test block compressive strength test, the surface of the test block and the test bench were wiped with a towel to remove debris and keep the compressed surface flat, and then the side length of the test block was measured with a ruler to calculate the area of the compressed surface. When testing, start the test with displacement, move at 0.25mm/min, and the target mode is load. After the setting is completed, the test block is placed in the center of the test bench, and then the iron piece is placed right above the test block. With the increase of load, it can be seen that the outer layer of the test block surface will gradually crack, then the inner crack, and finally be crushed. Load until the test block is damaged, record the maximum load when the test block is damaged.

According to the Chinese national standard “GB/T7617-1999 Test Method for Strength of Cementitious Sand”, the compressive strength of sludge biochar test block is calculated according to the following equation (1).

\[ R_c = \frac{F_c}{A} \]  

\( R_c \) is the compressive strength (Mpa); \( F_c \) is the maximum load when the specimen is damaged (N); \( A \) is the area of the compressed surface (mm²).

The specimens cured to age were tested for strength within 8 hours according to GB/T7617-1999 cementitious sand strength test method, and the uniaxial compressive strength test was carried out using TAW-2000 microcomputer-controlled electro-hydraulic servo rock triaxial testing machine with load as the starting mode and loading speed of 200N/S until the specimens were completely destroyed. Three replicate tests were performed for each biochar cement specimen at pyrolysis temperature to ensure the accuracy of the compressive strength test results.

2.3.2. Thermal Conductivity Test. Thermal conductivity testing was performed using TPS-1500 Hot Disk Thermal Standing Analyzer. In order to avoid the influence of water content in the specimen blocks cured in water to affect the thermal conductivity, resulting in large test results. Therefore, the thermal conductivity test was conducted by placing the specimens cured in water until the age of the specimens in a constant temperature blast drying oven at 30°C for 24 hours after ensuring that no cracks would be produced.

During the test, the surface of the prepared biochar cement test block was firstly polished smooth with rough sandpaper, then the Hot disk probe was fixed on the surface of the cement test block, and finally the measurement was started. The test parameters were set, the output power range was adjusted between 60-200mW, the time was controlled between 60s-200s, and at least three surfaces were selected for each test block. Finally, the average value of the measured data is taken and plotted. The thermal conductivity of the test block is calculated according to the following formula.

\[ \Delta T_{ave}(\tau) = \frac{P_0}{\alpha\pi^{1/2}} \cdot D(\tau) \]  

\( P_0 \) is the total power output from the probe, is the radius of the probe, is the thermal conductivity of the measured material, and \( D(\tau) \) is a dimensionless quantity as a function of time.
3. Results and Analysis

3.1. Effect of Biochar on the Compressive Strength of Cement

3.1.1. Effect of Curing Conditions on the Strength of Cement. Figures 1a-1b show the strength of the test blocks under wet and dry curing, respectively. From figure 1, it can be seen that the addition of biochar caused a significant increase in the strength of the test blocks. The strength of the wet cured specimens was much higher than that of the dry cured specimens, and the strength of the specimens after the addition of biochar was also higher than that of the dry cured specimens. It was also found that the difference in strength of the specimens with different dosing levels under dry curing conditions was more obvious, while there was no significant difference in the strength of the specimens with biochar cement at each pyrolysis temperature under the same dosing level. Thomas’s [2, 16] study concluded that cement hydration and admixture hydration reaction can be carried out continuously at relative humidity greater than 80%, while cement hydration reaction is difficult at relative humidity lower than 80%. Under wet curing conditions, there is sufficient moisture for the cement to carry out complete hydration reaction with high reaction rate, while the pore structure of biochar can absorb part of the free water for internal hydration of the cement, thus enhancing the strength of the test blocks. In contrast, when the test blocks are under low humidity conditions for a long time during dry curing, the capillaries inside the structure are extremely lack of water and the gel material cannot fully carry out the hydration reaction. Especially when the amount of cement is reduced with the increase of biochar admixture, because the hydration reaction produces less hydration products, the ability to combine with biochar and the sealing ability of its own pores is poor, thus affecting the denseness of the structure and leading to a significant decrease in strength. The insignificant difference in the strength of biochar cement specimens at each pyrolysis temperature under dry curing also indicates that the water retention of biochar and the volcanic ash activity of internal silica are also difficult to react with cement hydrates when the moisture is not sufficient to fully hydrate the cement for reaction.

3.1.2. Effect of Biochar Doping and Pyrolysis Temperature on Strength. In figure 1, it can be seen that the strength of the test blocks under both curing conditions decreased with the increase of biochar admixture, and the strength of the test blocks increased significantly at 1% admixture, and the strength of the test blocks of biochar cement at six pyrolysis temperatures increased on average by 51% (wet curing) and 15% (dry curing) compared with the blank control; the strength of the test blocks at 5% admixture increased on average by 11% in wet curing and decreased by 20% in dry curing. The worst strength performance was observed at 10% admixture ratio, with a 14% (wet curing) and 56% (dry curing) decrease in strength compared to the control. At small dosing, the cement hydration products can combine well with biochar, and the silica in biochar can react with the hydration products to produce a large amount of C-S-H gel to make the structure dense, and at the same time, it can fill and seal the pores of biochar, reduce water loss and optimize the water retention performance of biochar, so that the structural strength can be improved. The strength of the specimen with 1% doping at dry curing is still improved, which reflects the stability of biochar structure and water retention performance. On the other hand, when the amount of biochar is increased, the amount of cement is reduced, and the hydration products are reduced, which directly affects the structural strength on the one hand, and on the other hand, the less hydration products make it impossible to combine closely with biochar and produce pores, which affects the degree of structural denseness. This situation is more obvious under dry curing conditions where the cement cannot be fully hydrated, so the strength of dry curing specimens decreases more with the increase of admixture.
Figure 1. Compressive strength of biochar cement test block under different pyrolysis temperature and amount of substitution.

The pyrolysis temperature directly affects the carbon skeleton composition, pore structure, surface functional groups and other properties of biochar, and to a certain extent also affects the silicon content in biochar [2]. Therefore, the strength enhancement of the cement specimens with biochar at different pyrolysis temperatures had differences, and the best strength performance was 1% substitution ratio. Compared with the control CK, the strength of the cement specimens with biochar at six pyrolysis temperatures under wet curing increased by 37.27%, 39.75%, 61.04%, 52.10%, 60.33%, and 55.88%, respectively. The biomass pyrolysis was incomplete at the pyrolysis of 200°C and 300°C, and a large number of hydrophobic groups still existed on its surface, which affected the binding with the hydration products and made the strength improvement lower than the rest of the specimens. The physicochemical properties of biochar at pyrolysis temperatures greater than 400°C were similar, and the difference in strength enhancement of the test blocks was not significant, and the strength enhancement of the biochar cement test blocks at 400°C was slightly higher year-on-year.

Figure 2. Thermal conductivity of biochar cement block under different pyrolysis temperatures for different substitution ratios.

3.2. Effect of Biochar on the Thermal Conductivity of Cement

3.2.1. Effect of Maintenance Conditions on the Thermal Conductivity of Test Blocks. Thermal conductivity is one of the most important thermal and wet physical parameters of building materials,
and is a visual representation of the strength of thermal conductivity, indicating the heat flux per unit temperature gradient. A lower thermal conductivity is reflected by a lower rate of heat loss in the building structure, i.e., a better thermal insulation performance.

Figure 2 shows the thermal conductivity of biochar cement specimens under dry and wet curing. It can be seen that the addition of biochar reduces the thermal conductivity of the test blocks compared to ck, due to the pore structure of biochar and its inherent low thermal conductivity material. By comparing figures 2a-2b, the thermal conductivity of the dry cured test blocks is much lower than that of the wet cured cement test blocks. This phenomenon is basically caused by the following two aspects: one is that the humidity affects the thermal conductivity of the test blocks, and the thermal conductivity of moisture is stronger than that of cement material, and the thermal conductivity increases with the increase of humidity [14, 15]. On the other hand, the pore structure inside the test block and the pores of the biochar will block the heat transfer, resulting in a lower thermal conductivity. The reduction of the degree of hydration reaction and the evaporation of a large amount of free water during the drying and curing process will produce pores. Moreover, the degree of hydration also affects the combination of hydration products with biochar particles, which results in a large number of gaps around the biochar, as can be seen from the electron microscope images in figure 3. Therefore, the thermal conductivity of the dry cured specimens is much lower than that of the wet cured specimens in terms of thermal conductivity, which shows better thermal insulation performance.

3.2.2. Effect of Biochar Doping and Pyrolysis Temperature on the Thermal Conductivity of Test Blocks. In figure 2, the following pattern can be found: the thermal conductivity of the test blocks decreases with the increase of the doping amount in both dry and wet curing, and the lowest thermal conductivity is reached at 10% substitution ratio, and the thermal conductivity of the test blocks with different pyrolysis temperatures under dry and wet curing decreases by 36.21% and 27.62% respectively compared with the control CK. Even at 5% substitution ratio, the thermal conductivity of the test blocks decreased by 29.52% (dry curing) and 14.12% (wet curing). It indicates that the thermal insulation performance of the test blocks was greatly improved by the addition of biochar, and the higher the dosing amount, the more significant the performance improvement. From the experimental results, it was found that the thermal conductivity of the biochar cement test blocks with different pyrolysis temperatures at the same substitution ratio did not show a completely consistent trend, probably because the amount of biochar blending and the distribution of biochar inside different test blocks as well as the moisture content and the thermal conductivity of the test blocks had a The strength of this effect is greater than the difference in structural properties of biochar at different pyrolysis temperatures. However, through the experimental results, it can be theoretically concluded that the more the amount of biochar is used, the greater the room for improving the thermal insulation performance of the material, and this trend provides a good prospect for the use of biochar cement as a thermal insulation coating for building walls to improve the thermal insulation performance of walls.
Figure 3 shows the scanning electron microscope (SEM) images of biochar cement. In figures 3a-3b, it can be seen that the wet-cured specimen produced a large number of needle-like Ca(OH)\(_2\) crystals and flocculent C-S-H gels after the hydration reaction, while in the dry-cured case no crystals were produced due to incomplete hydration reaction, but the silica in the biochar reacted with the calcium and hydroxide ions in the hydration products to produce a large number of C-S-H gels. The binding of cement hydration products to biochar particles can be observed in the remaining electron microscopy images. Under wet condition, it can be seen in figures 3c-3e that there are fine grains around the biochar and the gel produced by hydration can seal part of the pores of the biochar, so that the free water absorbed by the biochar can be used for the internal hydration reaction, and at the same time, the accumulation and evaporation of free water are reduced, resulting in a dense structure. In contrast, it can be seen that only a small amount of gel is combined with the biochar under dry conditioning, and the combination with the biochar is not tight due to the insufficient hydration reaction of the cement itself, especially in the longitudinal section of the biochar, which is not blocked by the hydration products, thus forming a hydrophobic channel and also affecting the degree of structural compactness. From the electron microscope images in figure 3, it can be seen that the biochar and hydration products are more tightly bonded at 400°C, and the structure is denser due to the gel and crystallization filling around the biochar. During dry curing, the hydration reaction is not fully carried out, and the strength support of the test blocks is mainly from the hydration products of the hydration reaction, so the strength difference between the test blocks at each pyrolysis temperature with the same admixture is not prominent.
4. Conclusion

(1) Biochar blended into cement reduces the amount of cement, and the mass and density of test blocks decrease with the increase of blending amount, which can reduce the weight of the structure itself as a building material and optimize the building structure.

(2) The admixture of biochar increases the compressive strength of test blocks, but the strength of test blocks gradually decreases with the increase of admixture amount. At 1% substitution ratio, the strength of biochar cement specimens at each pyrolysis temperature in wet curing reached the maximum, with an average strength increase of about 50%; the strength of dry cured specimens increased by 15%. And the biochar cement specimens with the same amount of admixture at each pyrolysis temperature under wet curing showed obvious strength differences.

(3) Biochar blending into cement can improve the thermal insulation performance of the material. And the thermal conductivity decreases and the thermal insulation performance is enhanced with the increase of the admixture amount, reaching the optimum at 10%. The thermal insulation performance of the specimens under dry curing is better, and the thermal insulation performance of the specimens under dry and wet curing is improved by 39.21% and 27.62%, respectively. There was no significant correlation between the thermal conductivity of biochar cement specimens with the same amount of admixture and the pyrolysis temperature of biochar.

Taken together, the above conclusions show that the addition of biochar has improved the strength and thermal insulation properties of the cement. When the strength of the material is required to be high, a small amount of biochar can be used to enhance the structural strength, and when the material is used as a lightweight structure or when the heat insulation performance is emphasized, a large amount of biochar can be used, and at a substitution ratio of 5%, the heat insulation performance of the material can be significantly improved without affecting the structural strength. If this blending amount is promoted for national use, for every ton of cement produced, 80 kg of clay and 55 kg of coal will be saved, which will save about 5 million tons of coal every year and greatly reduce the emission of carbon dioxide, with considerable economic and environmental benefits.

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