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Research Article

Mechanical and Electrical Characteristics of Graphite Tailing Concrete

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The graphite tailing causes serious environmental pollution, and the pollution problem becomes worse and worse with the increase in graphite demands. This paper focuses on the graphite tailing concrete, which can alleviate the environment problem through utilizing graphite tailings. With the orthogonal experimental design, 16 groups of specimens were designed to investigate the compressive strength of the graphite tailing concrete, and each group had 6 specimens. The significance sequence of the influencing factors for the compressive strength was studied, including the ratio of water to cement, sand ratio, graphite tailings content, and carbon fiber content. The optimal contents of graphite tailings and carbon fiber were obtained from the further experimental study on the electrical characteristics of the graphite tailing concrete, and a regression analysis was conducted to develop the predictive mixture design relationships for the electrical resistivity of the conductive graphite tailing concrete. The experimental results show that the conductive concrete mixture containing graphite tailings and carbon fiber has satisfactory mechanical strength along with well electrical conductivity. With the increase in graphite tailings content, the compressive strength decreases slowly, but the electrical resistivity decreases much more obviously. Predictions with the proposed relationship are in reasonable agreement with experimental results. This study provides references for the graphite tailing utilization alleviating the environment problems.

1. Introduction

Graphite tailings are derived from froth flotation process of graphite ores [1]. With the increase in graphite production, the massive tailings containing hydrocarbon oil, diesel oil, and heavy metals have been generated during the past years in China, which pollute environment and occupy a large amount of land. The tailing dust flies with the wind, which causes serious air contamination. Most of the previous researches on graphite tailing mainly focused on the vanadium extraction, the evaluation of heavy metal pollution, and the preparation of foam concrete [2, 3]. It has been pointed out that the graphite tailings so far have not been effectively developed and utilized [4]. In this paper, the graphite tailing conductive concrete will be studied, which can utilize the graphite and alleviate environment problems.

Conductive concrete is a kind of heterogeneous material that is composited by binding and conductive materials, dielectric aggregates, and water [5]. The usage of electrically conductive concrete for deicing is a relatively new material technology, and the conductive concrete could pave way to heat roads [5], bridges [6], and airport [7, 8]. Paving a bridge deck with the electrically conductive concrete could also provide cathodic protection for the reinforcing steel [9]. In conductive concrete, conductive materials [10–12] that replace ordinary concrete aggregates provide with high electrical conductivity, and conductive materials usually include graphite, steel fiber, and carbon fiber [13]. Graphite has good electrical conductivity and pressure-sensitive characteristics, and it can be easily obtained in powder form [1]. Concrete added graphite powder will perform well conductivity, but former studies indicate that the strength of concrete will reduce rapidly with increasing graphite powder dosage [14]. When the graphite dosage is greater than 15%, the increase of the conductivity is not obvious, but the compressive strength decreases remarkably [15]. There is some graphite left in the graphite tailings, so the graphite tailings can provide conductive materials for the conductive concrete [1]. The additions of graphite tailings can reduce the electrical resistivity of concrete, and the tailings have less effect on the strength of concrete than pure graphite because the graphite fuses with rock. But the graphite content in tailings is limited, so another conductive material is needed to be added in the concrete to increase the conductivity.

Steel fiber and carbon fiber are other two conductive materials used in concrete usually [13]. The steel fiber-reinforced concrete is in many ways a well-known construction material, and its use has gradually increased over the last decades [16]. Yet the resistivity of steel fiber conductive concrete is not stable and changes with ages and environment. The alkaline environment in the concrete causes the steel fiber to produce a layer of passive film, which leads to the increase in resistivity, so steel fiber alone is unstable as conductive material [17]. The resistivity of carbon fiber is stable at high and low temperatures, and carbon fiber possesses a satisfactory corrosion resistance. In recent years, carbon fiber-reinforced polymer (FRP) materials in the form of fabrics and laminates have been motivated to use for retrofitting these corrosion-damaged reinforced concrete components [18]. The resistivity will be different with same carbon fiber if the uniform dispersal in concrete cannot be ensured, so the uniform dispersal of the carbon fiber is a key factor of using it as conductive material in concrete [13]. The use of a dispersive agent is necessary to disperse carbon fiber evenly in concrete [13, 19], but the carbon fiber as conductive material is stable. The tailings are easy to disperse in concrete, because graphite tailing size composition is even and the average particle size is 0.10 mm, which also will improve the uniform dispersal of the carbon fiber. Based on the above discussion, the steel fiber is not considered and the carbon fiber is adopted in the graphite tailing concrete as additional conductive material in this study, because the stability is a key issue for construction material.

Graphite tailing concrete can be applied as conductive concrete if the electrical resistivity is good enough [20], but mechanical properties of the graphite tailing concrete are the important factors in civil engineering. So the compressive strength should be studied at first. The orthogonal experimental design method has been adopted widely in civil engineering, such as construction material [21, 22] and structural optimization [23]. Orthogonal experimental design is the study of multifactor and level of design method, through the part of the test to find out the optimal level combination [24]. In this study, there are four key factors affecting the compressive strength of the conductive concrete including the ratio of water to cement, sand ratio, graphite tailings content, and carbon fiber content. It would require too many specimens with the full factorial design, so the orthogonal experimental design will be adopted for the compressive strength experimental study to reduce the required experimental specimens [25]. For the electrical characteristic experiment study, the four-electrode method will be adopted, which has been proved that it can provide more accurate measured results [26] than those with other measured methods.

In order to alleviate the environment problem through utilizing graphite tailings, the following studies are performed. Graphite tailings are added to the conventional concrete to make the conductive graphite tailing concrete, and carbon fibers are added to further improve the electrical conductivity. The effects of the ratio of water to cement, sand ratio, graphite tailings content, and carbon fiber content on mechanical characteristics are studied experimentally based on the orthogonal experimental design, and then, the electrical characteristics are studied with the four-electrode method. The optimal contents of graphite tailings and carbon fiber are studied, and the mixture design relationships for the electrical resistivity are predicted by regression analysis.

2. Experimental Materials

2.1. The Composition of the Graphite Tailings. The graphite tailing sample on experiment is obtained from a graphite mine in Jixi City, China. The chemical composition is analyzed with X-ray fluorescence, and the results are shown in Table 1.

The mineral composition of tailings was analyzed with X-ray diffraction mineral identification. The main mineral compositions of the tailings are quartz, grossular, lead bismuth vanadium oxide, graphite, and so on. Table 1 shows that the main composition of tailings is SiO_2, and there are also high levels of Al_2O_3 and CaO in the graphite tailing samples. From the chemical composition, it meets the basic requirements of concrete aggregate.

2.2. Other Experimental Materials. The cement used was Portland cement PI 42.5 provided by Harbin Swan cement factory, China. Standard river sand was used as fine aggregates. Crushed stone was used as coarse aggregates, and the particle size was no more than 20 mm. Chopped carbon fibers of 7 μm in diameter and 6 mm in nominal length were used as the additional conductive filler, and hydroxyethyl cellulose was used as the dispersive agent of carbon fiber. Defoamer was added to accompany hydroxyethyl, and the defoamer-cement ratio was 0.15% (by volume). The ratio of naphthalene superplasticizer to cement was 1% (by weight).

3. Compressive Strength

3.1. Orthogonal Experiment Design. There are four factors that affect the concrete mechanical and electrical properties to be investigated in this study: (A) water/cement material (W/C) ratio, (B) sand ratio, (C) tailings content, and (D) chopped carbon fiber content, and each factor has four

Table 1: Chemical composition of graphite tailings.

Composition	Fe_2O_3	MgO	Al_2O_3	SiO_2	CaO	K_2O	C	V_2O_5	Loss
Content (%)	5.073	2.326	10.205	62.498	15.547	2.26	1.13	0.308	0.653

different levels. Since the full factorial design requires 256 mixes, the orthogonal experimental design was adopted to reduce the number of mixes.

Orthogonal experimental design is based on the probability theory, the mathematical statistics, and the standardized orthogonal table. Orthogonal experimental design can select the right amount of representative samples from a large number of experimental designs to arrange experiments reasonably. To design an optimal test, it should have reasonable indicator and reference for selecting factor and the corresponding level. In this test, all the factors and corresponding levels are shown in Table 2.

The foundation of the orthogonal experimental design is the orthogonal table, and it forms as

$$\mathbf{L}_n\left(m^k\right), \tag{1}$$

where $\mathbf{L}$ is the symbol of the orthogonal table, n is the number of trials arranged by the orthogonal table (it is 16 in this study), m is the most number of factors arranged in the orthogonal table (it is selected to be 4 in this study), and k is the each factor level number to get the largest number in each single factor (it is selected to be 5 in this study).

According to the orthogonal experimental design table of $\mathbf{L}_{16}(4^5)$, a total of 16 mixes were tested. Tailings content was calculated by total weight. Carbon fiber content was calculated by total volume, and the density of carbon fiber is $1.76 \times 103\,\mathrm{kg/m^3}$. The details of the tested mixture composition per cubic metre are listed in Table 3. The target compressive strength is $40\,\mathrm{N/mm^2}$ when W/C is 0.49, the target compressive strength is $35\,\mathrm{N/mm^2}$ when W/C is 0.54, the target compressive strength is $30\,\mathrm{N/mm^2}$ when W/C is 0.60, and the target compressive strength is $25\,\mathrm{N/mm^2}$ when W/C is 0.49.

Hydroxyethyl was first added into water and left for 20 minutes letting it dissolve completely, and then carbon fibers and defoamer were added into water and stirred gently. The rest of the mixing water was poured into the mixer followed by the superplasticizer. Then, the cement was added and stirred by a rotary mixer for 3 minutes. The mixer was stopped, and the carbon fibers were poured into the mixer. When the mixer was run for 1 minute, the sand and the tailings were added and stirred for 3 minutes. Finally, the crushed stones were added and stirred for 3 minutes. After the mixture was poured into an oiled mold, the electrode (if applicable) was laid in fresh concrete. Then an external vibrator was used to facilitate compaction and decrease the amount of air bubbles. The samples were demolded after 24 hours and then cured under the standard condition at a temperature of 20°C and a relative humidity of 100% for 28 days [27].

The size of the concrete specimens for compressive strength tests was 150 mm × 150 mm × 150 mm, and each group with same mix proportion had 6 specimens for

Table 2: Factors and levels.

Level	W/C	Sand ratio (%)	Tailings content (%)	Carbon fiber content (%)
Level 1	0.49	30	0	0
Level 2	0.54	33	5	0.15
Level 3	0.60	36	10	0.30
Level 4	0.68	39	15	0.45

compressive strength tests as shown in Figure 1(a). Compressive strength was tested according to Standard for Test Method of Mechanical Properties on Ordinary Concrete (by Chinese Standard GB/T 50081-2002), and a servo-controlled hydraulic testing machine as shown in Figure 1(b) was used to apply a constant stress rate of 300 kPa/s.

3.2. Result Analysis. The compressive strengths are listed in Table 4, and the orthogonal experimental analysis is employed to obtain the optimal concrete mix [28]. The range analysis is conducted to evaluate the significance levels of all the influencing factors and select the optimal level of each factor. For range analysis, the Kam value and range value (R) are calculated as listed in Table 5. The Kam value for each level of a parameter is the arithmetic mean of four values of samples with the same level. For example, for concrete strength, the Kam 1 for parameter A is the arithmetic mean of concrete strength of samples with W/C of 0.49. The range value for each factor is the difference between the maximal and minimal values of the four levels, and the most significant factor has the highest R value. According to the R value, the most significant factor is tailings content, followed by W/C, and they have similar degree of influence. However, for sand ratio and carbon fiber content, the strength changes are insignificant (5.1% and 2.0% changes, resp.) as the parameter level changed.

Figure 2(a) shows the relationship between arithmetic mean of compressive strength and W/C. It shows that the arithmetic mean of compressive strength reduces 32.3% when the W/C increases from 0.49 to 0.68, which is consistent with target compressive strength and present researches [29, 30].

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Adopted sand ratio in the tests derives from the rational range of Standard for Test Method of Mechanical Properties on Ordinary Concrete, and the variations among levels are not very large as shown in Figure 2(b). It shows that the compressive strength decreases with the increase in sand ratio, but the differences are very small. It is consistent with

Table 3: The composition of the tested mixture per cubic metre.

Specimen	Water (kg/m^3)	Cement (kg/m^3)	Sand (kg/m^3)	Crushed stone (kg/m^3)	Graphite tailings (kg/m^3)	Carbon fiber (kg/m^3)
1	195	397.96	542.11	1264.93	0	0
2	195	397.96	556.72	1130.32	120	2.64
3	195	397.96	564.13	1002.91	240	5.28
4	195	397.96	564.35	882.69	360	7.92
5	195	361.11	517.17	1206.72	120	5.28
6	195	361.11	608.48	1235.41	0	7.92
7	195	361.11	534.2	949.69	360	0
8	195	361.11	625.52	978.37	240	2.64
9	195	325	492	1148	240	7.92
10	195	325	501.6	1018.4	360	5.28
11	195	325	676.8	1203.2	0	2.64
12	195	325	686.4	1073.6	120	0
13	195	286.76	467.47	1090.76	360	2.64
14	195	286.76	553.82	1124.42	240	0
15	195	286.76	647.36	1150.87	120	7.92
16	195	286.76	748.11	1170.12	0	5.28

(a) (b)

Figure 1: Compressive strength test. (a) Test specimen and (b) servo-controlled hydraulic testing machine.

Table 4: Compressive strength.

Specimen	W/C	Sand ratio (%)	Tailings content (%)	Carbon fiber content (%)	Compressive strength (N/mm^2)	Standard deviation of compressive strength
1	0.49	30	0	0	43.7	1.315
2	0.49	33	5	0.15	41.2	0.834
3	0.49	36	10	0.30	39.6	0.942
4	0.49	39	15	0.45	31.2	0.994
5	0.54	30	5	0.30	38.5	0.529
6	0.54	33	0	0.45	42.6	1.227
7	0.54	36	15	0	24.9	1.058
8	0.54	39	10	0.15	34.3	0.962
9	0.60	30	10	0.45	32.9	1.183
10	0.60	33	15	0.30	24.3	0.752
11	0.60	36	0	0.15	35	0.617
12	0.60	39	5	0	31.6	0.897
13	0.68	30	15	0.15	20.4	0.825
14	0.68	33	10	0	22.8	0.529
15	0.68	36	5	0.45	30.9	0.776
16	0.68	39	0	0.30	31.3	1.269

the present common results of study that sand ratio mainly has effect on the workability of concrete and has little effect on compressive strength. The graphite tailings can also serve as part action of fine aggregates, so it leads to that the sand ratio is near 30% in the experiment which makes the compressive strength to be higher with enough workability.

Table 5: Range analysis on compressive strength (N/mm^2).

Factors	W/C	Sand ratio	Tailings content	Carbon fiber content
Kam 1	38.925	33.875	38.15	30.75
Kam 2	35.075	32.725	35.55	32.725
Kam 3	30.95	32.6	32.4	33.425
Kam 4	26.35	32.1	25.2	34.4
R	12.575	1.775	12.95	3.65

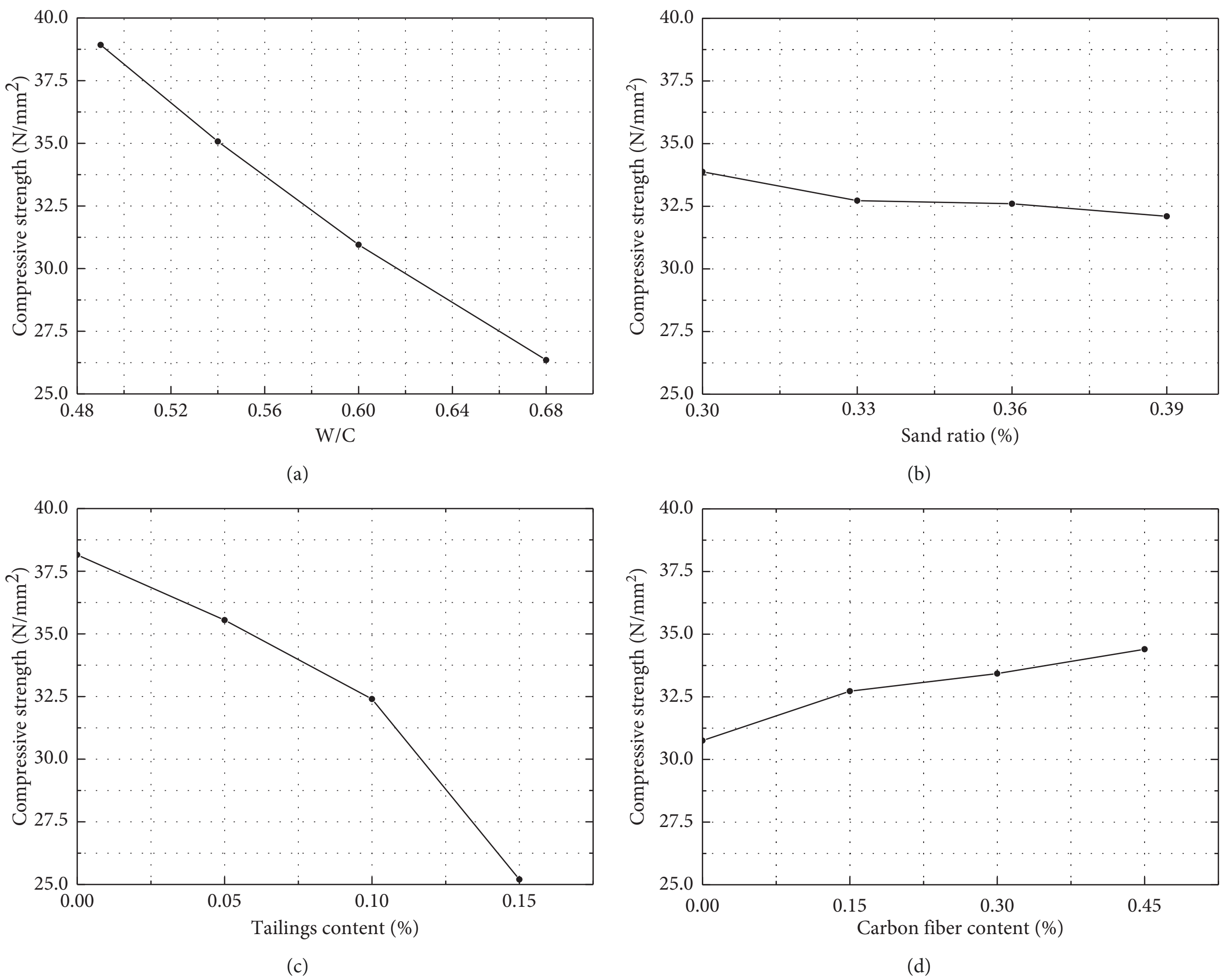


Figure 2: Relationship between compressive strength and affecting factors. (a) W/C; (b) sand ratio; (c) tailings content; (d) carbon fiber content.

The arithmetic mean of compressive strength decreases with the increase of graphite tailings content as shown in Figure 2(c). In the beginning, the degradation of compressive strength is not very fast. The strength of concrete will reduce rapidly if the graphite tailings content is greater than 10%. Graphite tailings also contain some free graphite and hydrocarbon oil which will lead to degradation of strength rapidly. When tailings content is 10%, the relationship between compressive strength and target strength is listed in Table 6, which is extracted from Table 4. The compressive strength does not reduce too much with respect to the target strength because compressive strength can be slightly improved by carbon fiber.

The chopped carbon fibers have a little reinforcing effect on compressive strength as shown in Figure 2(d). It is rod-like or mesh-like long carbon fibers that have been heretofore used for a carbon fiber-reinforced concrete, and short carbon fibers are used only for mortar containing no coarse aggregate or spraying repair material. One reason is that the carbon fibers are damaged when the carbon fibers are incorporated in the form of short fiber into a concrete containing a coarse aggregate. Even if the chopped carbon fibers are used, the

Table 6: Compressive strength and target strength.

Specimen	W/C	Tailings content (%)	Compressive strength	Target strength	Compressive strength (%)
3	0.49	10	39.6	40	−1.0
8	0.54	10	34.3	35	−2.0
9	0.60	10	32.9	30	9.7
14	0.68	10	22.8	25	−8.8

mechanical effect is only to prevent development of cracking that already occurred. The other reason is that the bonding between the carbon fibers and the cement matrix is not strong enough. In order to improve strength, it is important to have good bonding between the carbon fibers and the cement matrix. The carbon fiber surface is coated with a layer of epoxy resin. The layer of epoxy resin makes the chopped carbon fibers to easily slip out from a cement matrix.

4. Electrical Characteristics

4.1. Experiment Design of Four-Electrode Method. The size of the specimens for electrical properties was 150 mm × 150 mm × 300 mm. Each group with the same mix proportion had 3 specimens for electrical property tests. The effect of W/C and sand ratio on the resistivity of conductive concrete is very limited and complex relative to conductive materials. According to the previous study and target compressive strength of 30 N/mm^2, W/C and sand content were 0.6 and 30%, respectively. Carbon fiber volume was from 0.0 to 0.45%, and tailings content was from 0 to 15%.

The selection and arrangement of electrodes significantly affect the experiment on conductive properties. There are several test methods for measuring the electrical resistivity of concrete such as two-electrode method [13] and four-electrode method [28]. The two-electrode method includes posted outside methods (sticking graphite cloth or outer sticky copper electrodes) and embedded methods (embedded stainless steel sheet or steel mesh electrodes). The four-electrode method embeds four stainless steel sheets or steel mesh electrodes in parallel within the concrete. The four-electrode method can eliminate contact resistance and is recognized as a suitable and reliable method for testing resistivity [31]. The four-electrode technique was selected for this study to measure the electrical resistivity of specimens.

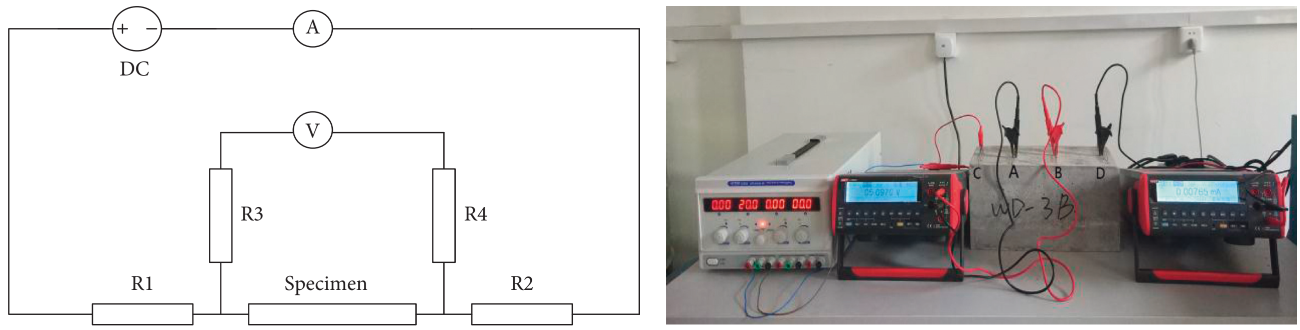
The electrical schematic of the four-electrode method is shown in Figure 3(a), and the electrical resistivity measurement in the lab is shown in Figure 3(b). Four parallel steel mesh electrodes are installed into the specimens as electrodes, and the mesh size is 25 mm × 25 mm to fit the coarse aggregate as shown in Figure 3(b). The distance between the electrode and the edge of the mold ranges from 15 mm to 20 mm, and the length of the electrode out of the concrete is 30 mm. Two electrodes (C and D) in the two sides of the specimen deliver current I_{AB} into the system, whereas the other two electrodes (A and B) detect the voltage U_{CD}. The ratio between voltage U_{CD} and current I_{AB} can be used to determine the electrical resistivity of specimens.

4.2. Result Analysis. As shown in Figure 4, the increase of graphite tailings can obviously decrease the electrical resistivity of specimens. The decrease of resistivity will slow down when carbon fiber content is more than 0.3% if the graphite tailings content is held constant. The addition of conductive components in the concrete, such as carbon fiber and graphite tailings, can significantly improve the electrical conductivity of concrete while maintaining good mechanical properties. The increase in conductive materials facilitates the formation of conductive networks, which overlap with one another to decrease concrete resistivity. In concrete, current is conducted by electrons or holes in the conductive network and tunnels over the substrate barrier. As the dosage of the conductive component increases to a critical value, the conductive networks expand to a certain range to form conductive paths, thus decreasing the resistivity of conductive concrete. When the dosage of conductive materials exceeds the threshold, the amplitude of reduction significantly diminishes although the resistivity of the conductive concrete continues to decrease [13].

From an economic view, the optimum dosage of conductive materials should approach the percolation threshold. So, an appropriate percentage of carbon fiber is 0.3% if the requirement for electrical resistivity is not very high. To get better conductivity, graphite tailings can be added more to the concrete if the concrete can satisfy the demand for strength. This experimental study shows that the appropriate percentage for tailings is 10% for good enough strength.

The electrical resistivity can be lower than 1 kΩ·cm as shown in Table 7, and graphite tailing concrete can be used in deicing or snow melting [32]. If the electrical resistivity is high, it will not generate heat effectively. A regression analysis of measured resistivity data in Table 7 is conducted to predict electrical resistivity of concrete. Two variables are examined, including tailings content and carbon fiber content. W/C and sand content keep constant and are 0.6 and 30%, respectively. The fitted equation is shown as follows:

$$R = 20.72 + 0.9452\left(\operatorname{arccot}\left(7.86 - 40.94C_{cf}\right)\right)^3 + \frac{419100}{\left(C_{gt} + 34.79\right)^{2.5}} + 0.01377C_{gt}^2 - 37.75C_{cf} + 0.523\left(C_{cf}C_{gt}\right)^{1.6}, \quad (2)$$



(a)

(b)

Figure 3: The measurement circuit of the four-electrode method. (a) Electrical schematic with electrical connections and (b) electrical resistivity measurement with the four-electrode method.

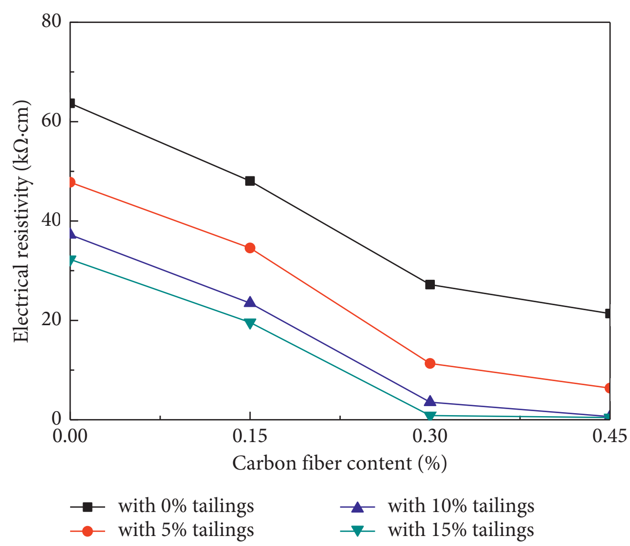


Figure 4: Electrical resistivity with different tailings content and carbon fiber content.

Table 7: Measured resistivity and estimated resistivity.

Specimen	Tailings (%)	Carbon fiber (%)	Measured resistivity (kΩ·cm)	Estimated resistivity (kΩ·cm)	Relative error (%)
1	0	0	63.68	63.805	−0.20
2	5	0	47.8	47.408	0.82
3	10	0	37.24	37.692	−1.21
4	15	0	32.28	32.156	0.38
5	0	0.15	48.04	49.163	−2.34
6	5	0.15	34.56	33.096	4.23
7	10	0.15	23.48	24.050	−2.43
8	15	0.15	19.6	19.429	0.87
9	0	0.3	27.2	26.672	1.94
10	5	0.3	11.32	11.276	0.39
11	10	0.3	3.53	3.591	−1.74
12	15	0.3	0.837	0.826	1.32
13	0	0.45	21.36	21.000	1.69
14	5	0.45	6.36	6.517	−2.47
15	10	0.45	0.643	0.689	−7.16
16	15	0.45	0.435	0.453	−4.06

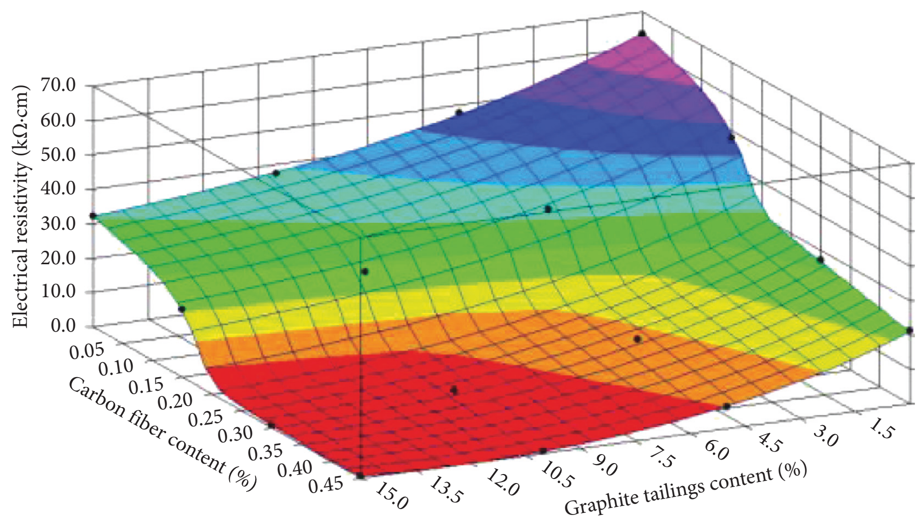


FIGURE 5: Electrical resistivity results with proposed regression equation.

where R is the electrical resistivity (kΩ·cm), C_{gt} is the graphite tailings content (%), and C_{cf} is the carbon fiber content (%).

An inverse trigonometric function is used to simulate threshold effect of electrical resistivity. The comparison between measured resistivity and estimated resistivity is shown in Table 7 and Figure 5. The maximum of relative errors is 7.16%.

Predictions with the proposed relationship are in reasonable agreement with experimental results measured by the four-electrode method. Fitting curved surface is rational and acceptable at not only experimental points but also transitional regions.

5. Conclusions

This paper proposed the method of the graphite tailing utilization for conductive concrete, and the compressive strength and electrical conductivity of the conductive concrete are investigated by test. The conductive concrete mixture containing graphite tailings and carbon fiber shows a good electrical conductivity and an enough mechanical strength. Some of the conclusions from the study are as follows:

(1) For graphite tailing concrete, it is more reasonable that the sand ratio is near 30% so that compressive strength is high enough with good workability.

(2) The compressive strength decreases with the increasing graphite tailings content. When tailings content is 10%, the compressive strength does not reduce too much with respect to the target strength because compressive strength can be slightly improved by carbon fiber.

(3) The increase of graphite tailings can obviously decrease the electrical resistivity of specimens. Graphite tailing concrete can be used in deicing or snow melting. From an economic view, an appropriate percentage for carbon fiber is 0.3% if the requirement for electrical resistivity is not very high.

(4) Predictions with the proposed relationship are in reasonable agreement with experimental results measured by the four-electrode method. Fitting curved surface is rational and acceptable at not only experimental points but also transitional regions.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; and in the decision to publish the results.

Conflicts of Interest

The authors declare no conflicts of interest.

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