Analysis of pH and Conductivity Variation Characteristics of Coal Gangue Used in Freeway Subgrade and Its Correlation

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Abstract. Coal gangue is a common solid waste in coal mining area, which causes great environmental pollution. Using coal gangue as filling material of highway subgrade can turn waste into treasure. In order to study the greening situation of the road section with coal gangue instead of soil as subgrade filling material, the pH and electrical conductivity (EC) were studied. The electrical conductivity (EC) and pH value of coal gangue used in a highway subgrade test section under different soaking time and initial pH solution were measured, and their change characteristics were analyzed. Both of them increased with the extension of time, and the change trend of EC was more severe. The results of correlation analysis showed that pH and EC were highly positively correlated, and the correlation coefficients were 0.7941, 0.8198 and 0.8639 at initial ph 4.1, 5.2 and 6.5, respectively. On the whole, pH is proportional to EC. By mastering the change characteristics and correlation between pH and conductivity of coal gangue under different pH conditions, it can provide certain data and theoretical support for the greening research of coal gangue as subgrade filler.

Keywords: Freeway; Gangue ; pH ; Electrical conductance, EC; Correlation analysis.

1. Introduction
Coal is the main energy storage in China, and the amount of coal gangue discharged in the process of coal mining and coal washing is increasing year by year. At present, the utilization rate of coal gangue in China is low. Most of the coal gangue is dumped and piled around the mining area without treatment, forming a large number of coal gangue hills, occupying land and bringing serious environmental pollution [2-5]. The long-term open-air waste dump has a large amount of accumulation and produces harmful gases such as sulfur dioxide due to spontaneous combustion, which pollutes the atmosphere; after leaching, it may also pollute soil and groundwater. In the process of highway construction, filling subgrade needs a lot of earth and stone resources. Filling the subgrade with coal gangue can reduce soil sampling, consumption of coal gangue and land occupation. It is a method to turn coal gangue into treasure [6-8], which is a comprehensive utilization way suitable for China's national conditions.
However, when coal gangue is used as subgrade filler instead of soil, it should be noted that coal gangue is not suitable for crop growth due to extremely poor soil, high or low pH, low water holding capacity, easy erosion and poor soil microbial activity [9-11], which is the most important limitation. The factor is that the pH value of coal gangue is too high or too low, which can not meet the basic growth requirements of crops. Electrical conductivity (EC) is contributed by the water-soluble ion components in the soaking solution, and its size reflects the total ion concentration in precipitation [12]. In pedology, EC is the threshold to limit the activity of plants and microorganisms, which will affect the transformation, existing state and availability of nutrients and pollutants [13], and is the basic index reflecting electrochemical characteristics and fertility characteristics. Through the determination of EC, salt concentration and water status can be mastered timely and effectively, which has theoretical significance for rational utilization of soil [14]. Coal gangue is used as subgrade material instead of soil. The greening situation along the relevant road section needs to be paid attention to, so it is of practical significance to study the EC of coal gangue.

In this research, the coal gangue used in a highway subgrade test section was extracted by different pH solutions to monitor the continuous changes of pH and EC after long-term water leaching, so as to find out the pH and EC of coal gangue in the real environment. And the correlation between the two is analyzed to provide certain data and theoretical support for the greening research under the condition of coal gangue as subgrade filler.

2. Materials and methods
The coal gangue used in the experiment is taken from the materials used in the test section of an expressway, and the pH and EC status of the gangue are investigated by directly soaking the limit case of natural leaching [15-16]. According to the local meteorological data [17], the longest continuous rainfall time of the experimental section for many years is 20 days. Based on 0.5, 1 and 2 times of the 20 days, three times of 10 days, 20 days and 40 days are obtained. Due to the large amount of dissolution at the initial stage of soaking, it will increase by 1 day, 3 days and 6 days. Therefore, the soaking time is 1 day, 3 days, 6 days, 10 days, 20 days and 40 days. The average pH of precipitation in the construction area is 5.2, the minimum pH is 4.1, and the average pH of water body near the construction site is 6.5. Distilled water was used as mother liquor and dilute nitric acid was used to adjust pH. Put the coal gangue sample into the container, add the solution with different pH according to the ratio of solid to liquid 1:5, and let the coal gangue soak for a certain period of time. At the same time, the pH and EC Value of the dissolved liquid should be measured and recorded. PH of the sample was determined by phs-828-s pH meter and EC was determined by DDS-307A conductivity meter.

3. Results and Discussion
3.1. PH change of coal gangue

| initial pH | soaking time/days |
|-----------|------------------|
|           | 1    | 3    | 6    | 10   | 20   | 40   |
| 4.1       | 5.54 | 6.14 | 6.64 | 6.68 | 7.16 | 7.25 |
| 5.2       | 5.75 | 6.40 | 6.74 | 6.75 | 6.76 | 7.39 |
| 6.5       | 6.57 | 6.60 | 6.75 | 7.03 | 7.18 | 7.31 |

The variation trend of pH of the dissolution solution with time is shown in Table 1. It can be seen that no matter the initial pH of the dissolution solution is 4.1, 5.2 or 6.5, the pH of the dissolution solution is rising throughout the experimental process, and the pH of the dissolution solution is stable at about 7.3 after 40 days, showing weak alkalinity. No matter what the initial pH value of the leaching solution, the coal gangue used in the experiment has no great influence on the final pH value of the
leaching solution. The pH of Coal Gangue Leaching Solution in subgrade test section depends on its material composition, and is not affected by rainwater pH or other external environment. Iron sulfide is an important reason for the low pH of Coal Gangue Leaching Solution [18]. This is because the oxidation of iron sulfide in the soaking process will produce H$_2$SO$_4$, which will increase the acidity of the solution. The specific chemical reaction formula is as follows:

$$4\text{FeS}_2 + 15\text{O}_2 + 14\text{H}_2\text{O} = 16\text{H}^+ + 8\text{SO}_4^{2-} + 4\text{Fe(OH)}_3$$

In addition, the sulfate and organic sulfur contained in coal gangue can also reduce the pH value of the solution. The coal gangue used in the test is coal-fired gangue, which has been exposed to the air for a long time with high weathering degree, and is often washed by rain water. The matrix composition has been stable, in which sulfur dioxide is oxidized to produce SO$_2$. The content of metal sulfide in coal-fired gangue is already very low, and the concentration of H$^+$ produced is limited. Therefore, the pH value of leaching solution increases. Ca, Mg, K, Na and other metal compounds in coal gangue will react with H$^+$ to make the solution alkaline [19-20]. In addition, the nitrogen-containing substances in coal gangue dissolve and ionize NH$_4^+$, forming an alkaline environment [21-22]. The alkaline reaction is the dominant factor in the coal gangue, so even if the initial dissolution solution is acid solution, the final dissolution solution will return to weak alkalinity. In the first 10 days of immersion, the pH value increased rapidly, which indicated that the reaction speed of alkaline substances was fast, and then reached a relatively stable state. During the soaking time of 40 days, the overall pH value did not decrease. Some studies think that [23] this is mainly because the carbonic acid system plays a buffer role in the leaching process, so that the pH value of the solution is maintained within a certain range. The pH value of weathered coal gangue is relatively stable, which is more convenient for reasonable treatment and utilization [24].

The weathering characteristics of coal gangue and the mineral composition and characteristics that determine the soil forming mechanism are the basis for determining plant species and cultivation methods. Coal gangue is generally a large stone, after years of weathering particles become smaller. The aggregate structure is the basis of determining soil fertility level. Although the weathering degree of coal gangue is good, the gravel or stone with larger particle size still accounts for a large proportion, which determines the poor cultivability of coal gangue, poor water and fertilizer retention capacity, water and nutrient loss easily, and it is difficult to plant vegetation. On the other hand, coal gangue has good aeration and water permeability, and plant roots are easy to grow and expand to the depth of coal gangue [25].

### 3.2. Changes of EC in coal gangue

| initial pH | EC/MS/cm |
|------------|----------|
|            | 1  3  6  10 20 40 |
| 4.1        | 2.582 3.533 3.794 2.9715 |
| 5.2        | 2.292 3.826 3.693 3.144 2.2658 |
| 6.5        | 2.2 2.412 3.532 3.823 3.89610 |

The variation trend of EC Value of leaching solution with time is shown in Table 2. It can be seen from the figure that the EC Value of different coal gangue has little difference in the initial stage of soaking, ranging from 2.2 to 2.58 MS/cm. With the prolongation of soaking time, the EC values of coal gangue under three initial pH values showed the same change trend, showing a significant increase trend. After soaking for 40 days, the EC Value of coal gangue is still rising. The change trend of EC of coal gangue is similar to that of pH, but the trend of EC is more intense. Since EC is the reaction of salt ion concentration in matrix solution, the higher the EC value is, the better the...
conductivity of solution is, and the higher the base ion concentration is [26]. The coal gangue is greatly affected by the external environment. The degree of weathering and leaching is high, and the leaching loss is large. Under the soaking condition, the release of residual salt ions is easier and the stability is faster.

3.3. Correlation analysis of pH and EC of coal gangue
In order to evaluate the correlation between pH and EC of coal gangue, the correlation analysis of pH and EC under different initial pH solution soaking conditions was carried out. The results show that when the initial pH value of the soaking solution is 4.1, the pH and EC Value of coal gangue have a significant positive correlation, the correlation coefficient is $r = 0.7941$, and the linear correlation equation is $y = 2.0431x - 9.3965$; when the initial pH value of the soaking solution is 5.2, the pH and EC Value of coal gangue have a significant positive correlation, the correlation coefficient is $r = 0.8198$, and the linear correlation equation is $y = 2.5023x - 13.044$ Under the condition of 6.5, the pH value and EC Value of coal gangue have a significant positive correlation, the correlation coefficient is $r = 0.8639$, and the linear correlation equation is $y = 4.118x - 25.117$. With the increase of initial pH, the correlation coefficient of pH and EC value also increased, and the positive correlation between them was more obvious. This indicates that the difference of correlation between pH and EC of coal gangue can also reflect the different leaching environment to some extent. On the whole, pH is proportional to EC. Some studies have shown that the correlation between pH and EC Value of [24] coal gangue is closely related to the weathering degree of coal gangue. The higher the weathering degree is, the better the positive correlation is, which is consistent with the actual situation of high weathering degree of coal gangue used in our experiment.

4. Conclusion
(1) No matter the initial pH of the dissolution solution is 4.1, 5.2 or 6.5, the pH of the dissolution solution is rising. After 40 days, the pH of the dissolution solution is stable at about 7.3, showing weak alkaline. The pH value of Coal Gangue Leaching Solution in subgrade test section depends on its own material composition, and is not affected by rainwater pH value or other external environment. The change trend of EC of coal gangue is similar to that of pH, but the trend of EC is more intense.

(2) After the coal gangue is discharged, it is better to stack the gangue for a period of time in the natural state. After a certain degree of weathering and leaching, it is better to use the coal gangue for agriculture after its pH and EC value are stable. On the premise of good anti-seepage, anti spontaneous combustion and environmental protection, it can be combined with measures to accelerate the weathering of coal gangue, which will greatly reduce the cost of coal gangue matrix improvement.

(3) In this experiment, the measured values of EC and pH of coal gangue used for highway subgrade were measured under different initial pH solutions, and the correlation analysis was conducted between the two values. The correlation coefficients $r$ of pH and EC and pH were 0.7941, 0.8198 and 0.8639 respectively under the conditions of initial pH 4.1, 5.2 and 6.5, respectively. It shows that the pH value of coal gangue has a positive correlation with EC, and the weathering degree of coal gangue is also Higher.

Acknowledgements
The authors are grateful for financial support by Science and Technology Project in Department of Transport of Shandong Province (2019B24), Science and technology R & D program of CSCEC (CSCEC-2020-Z-52) and Shandong Province local road network traffic construction standardization demonstration intelligent promotion demonstration construction project (C1940). The contributions of the manuscript reviewers is also acknowledged.

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