Research Article

Curing Effect and Resistivity Evolution of Zinc-Contaminated Red Clay Cured by Phosphate-Based Binder

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Curing agent is often used in the in situ remediation of industrial contaminated sites. The reaction between curing agent and contaminated soil has a great impact on the conductivity of soil. Quantitative analysis of the resistivity evolution of cured contaminated soil is an important prerequisite for the accurate evaluation of the in situ remediation effect of heavy metal contaminated sites. In this paper, the pH value, unconfined compressive strength, and resistivity evolution of Zn-contaminated red clay cured with new phosphate-based binder (KMP) at different curing ages were tested, and the internal relationship between the KMP content and the metal ion content and the pH value, unconfined compressive strength, and resistivity evolution were analyzed. The curing effect of KMP, Zn²⁺ concentration, and curing age on contaminated soil was further evaluated. The results show that the unconfined compressive strength of red clay is weakened with the increase of Zn²⁺ concentration. The curing effect of KMP on zinc-contaminated red clay is obvious. The pH control of KMP curing agent on zinc-contaminated red clay is effective, and the pH value within 10.5 can effectively stabilize metal ion leaching. There is a good linear relationship between KMP content and curing age and resistivity. Under uniaxial compression, the resistivity decreases with the increase of stress at different Zn²⁺ concentrations, and the minimum value of the resistivity corresponds to the peak value of uniaxial compression. It provides possibility for the application of resistivity method in the study of mechanical strength properties of red clay.

1. Introduction

Under the background of the promotion of ecological civilization construction and industrial development and upgrading, many enterprises with serious environmental pollution have closed down, but the remaining pollution problem still exists. At present, the noticeable problem is the site pollution caused by heavy metals (such as zinc and cadmium). Heavy metal pollution of soil not only causes damage to the ecosystem and threatens the lives of surrounding residents but also changes the engineering nature and structure of the soil and brings challenges to engineering construction [1, 2]. Red clay, which is widely distributed in southwest China, is rich in iron oxides, with a high porosity ratio, high liquid limit, high bearing capacity, and low compression and complex strength properties. These special physical and mechanical characteristics make the assessment and restoration of heavy metal contaminated sites in this region special [3–8]. Therefore, there is an urgent need to carry out the assessment of contaminated sites and propose corresponding remediation and disposal measures.

At present, the solidification/stabilization method is widely used for the remediation of heavy metal-contaminated soil. Studies have shown that traditional curing agents such as cement, blast furnace slag-MgO, and fly ash can greatly improve the strength of contaminated soil, but there are still many disadvantages; for example, the cured body has more capillary pores after treatment, which makes the heavy metals in the cured body easy to desorption and the treatment has a great impact on the environment.
that is not conducive to further ecological restoration [9–12]. In recent years, phosphate-based binder has attracted widespread attention due to their low price, good remediation effect, and stable chemical properties for stabilizing heavy metal-contaminated soils. Scholars have also carried out fruitful explorations on them [13–16]. Compared with the traditional cement-based curing agent, which is mainly cured through wrapping and surface adsorption, phosphorus-containing stabilizers have high curing stability and are less affected by the environmental pH value. The fixation of Zn$^{2+}$ by phosphate-based binder is mainly by surface adsorption, coprecipitation, and complexation. Kumpiene et al. [17] have shown that the fixation mechanism of phosphorus-containing stabilizers for heavy metals is mainly based on surface coordination, ion exchange, or formation of amorphous substances, accompanied by precipitation. Cao et al. [18] found that Zn$^{2+}$ ions would be fixed by surface adsorption and complex cooperation and then formed insoluble substance precipitation. The adsorption mechanism of Zn$^{2+}$ is that Zn$^{2+}$ forms complexation with POH groups on the surface of apatite. In addition, Ca$^{2+}$ in phosphate will also precipitate with Zn$^{2+}$. McGowen et al. [19] pointed out that Zn can react with phosphate to form zinc phosphate salts that are less soluble, to achieve the immobilization effect. However, there is still a lack of research on KMP curing agent using acidification pretreatment of phosphate rock powder to fix heavy metal ions in red clay.

Current assessments of the effectiveness of solidification and stabilization of heavy metal contaminated soils are usually based on chemical and mechanical tests. Although such traditional methods can obtain accurate test results, they need to drill sampling on the spot and carry out indoor testing, which leads to large time and testing cost. In order to overcome the shortcomings of traditional methods, many scholars have proposed to evaluate the pollution and in situ restoration effect of polluted sites based on geophysical exploration methods. The resistivity method is widely used in geophysical exploration due to its simple operation and easy implementation [20–24]. Ya et al. [25] used ERI technology to discuss the resistance evolution law of heavy metal contaminated sites. Azhar et al. [26] studied the migration of heavy metals in underground soil by using resistivity method and profile analysis. Hazreek et al. [27] established the correlation between physical indexes and resistivity of zinc-contaminated soil through laboratory tests. Ly et al. [23] discussed in detail the influence of curing age and heavy metal concentration on the soil resistivity characteristics and confirmed that a good linear relationship existed among resistivity, curing age, and unconfined compressive strength [28]. Resistivity is one of the inherent properties of soil and has a good correlation with the macro characteristics of soil [29]. To reveal the resistivity evolution mechanism of solidified heavy metals, the use of resistivity method could quickly and conveniently realize the nondestructive evaluation of the repair effect of solidified and stabilized heavy metal contaminated sites. However, the correlation between the effect of KMP curing agent in curing heavy metal ions and resistivity has not been fully established.

In this paper, the pH value, compressive strength, and resistivity of KMP-cured zinc-contaminated red clay at different curing ages were tested, and the intrinsic correlation of KMP content and curing age on pH, compressive strength, and resistivity of zinc-contaminated red clay was explored, to provide basic data for the evaluation of resistivity method for solidification and stabilization of heavy metal contaminated sites.

2. Materials and Methods

2.1. Test Materials. The red clay used in the test was taken from Yanshan Town, Guilin City, China, at a depth of approximately 3 m. It was brown-red, with the initial moisture content of 6.3%. In the test, the red clay was air-dried and then crushed to pass through a 2 mm soil sieve. The basic physical properties of red clay are shown in Table 1. In this experiment, the Zn$^{2+}$-contaminated solution is a Zn(NO$_3$)$_2$ solution prepared by Zn(NO$_3$)$_2$·6H$_2$O crystal and deionized water.

The curing agent used in the test is KMP, a phosphorus-containing curing agent. The preparation method is as follows: mix 1 mol/L oxalic acid solution with phosphate ore powder according to the liquid-solid ratio of 1:2. After 48 hours of rest, dry and crush the mixture to obtain acid phosphorus ore powder. Then, the mixed phosphorus acidified ore powder, KH$_2$PO$_4$, and MgO are mixed according to the mass ratio of 1:1:1.2, crushed and sieved by 1 mm to obtain the KMP curing agent.

The Zn$^{2+}$ concentrations of 0.1%, 0.5%, and 1% were denoted as Zn0.1, Zn0.5, and Zn1. The KMP content of 4%, 6%, and 10% was denoted as K4, K6, and K10, respectively. The curing age is set as 1 d, 7 d, 14 d, and 28 d to explore the relationship between curing time and resistivity. The experimental variables are shown in Table 2 (the longitudinal variable is the KMP content, and the lateral variable is the Zn2+ concentration).

2.2. Specimen Preparation.① Contaminated soil preparation. The red clay was dried and crushed, passed through a 2 mm sieve and then placed in an oven for drying at low temperature. Zinc nitrate solution was prepared with deionized water, and the Zn$^{2+}$ content was 0.05%, 0.10%, and 0.50% (the content of zinc ions is the mass ratio of zinc ions to soil particles). The initial water content was fixed at the red clay’ optimum moisture content of 30.8%. The prepared soil samples were sealed and passivated for 10 days after

<table>
<thead>
<tr>
<th>Liquid limit/%</th>
<th>Plastic limit/%</th>
<th>Plasticity index</th>
<th>Optimum moisture content/%</th>
<th>Maximum dry density/(g/cm$^3$)</th>
<th>Specific gravity</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.7</td>
<td>33.2</td>
<td>17.5</td>
<td>30.8</td>
<td>1.53</td>
<td>2.72</td>
<td>4.67</td>
</tr>
</tbody>
</table>
stirring evenly. ② Curing agent addition. After artificially preparing the heavy metal contaminated red clay, the prepared KMP curing agent is added according to the designed dosage (4%, 6%, and 10%, the curing agent accounts for the mass percentage of dry soil) and fully stirred until there are no obvious white particles. Then, the contaminated red clay mixture mixed with curing agent was wrapped and sealed with an airtight bag to prevent water evaporation and placed in a standard curing chamber for curing 24 h. ③ Preparation of specimens. According to the Standard for Soil Test Method [30], the reconstruction triaxial shear specimen (diameter 39.1 mm and height 80 mm) was prepared according to the dry density of 1.40 g/cm³ and the initial moisture content. The compaction method is adopted, and the compaction is divided into 4 layers. ④ Specimens maintenance. After each layer is compacted, the surface is anchored, and the next compaction is performed. The specimen is obtained after 4 times of compaction. The curing time is calculated after the specimen is placed in the standard curing chamber.

2.3. Test Methods

2.3.1. Unconfined Compression Strength Test. The unconfined compressive strength test equipment adopts the DW-1 unconfined compression apparatus. The maximum axial load is 0.6 kN, the loading rate is 2 mm/min, and the force ring coefficient C is 2.139 N/0.01 mm. The unconfined compression strength can be calculated by the following equation:

\[
\sigma = \frac{C \times R}{A} \times 10.
\]

In the formula, \( \sigma \) is the axial stress (kPa); \( A \) is the cross-sectional area of sample (cm²); \( C \) is the coefficient of dynamometer (N/0.01 mm); \( R \) is the dynamometer reading (0.01 mm).

2.3.2. pH Test. The pH value of the contaminated soil suspension was tested by the PHS-3C instrument. To prepare the soil suspension, the pH value is measured according to the instrument manual with an accuracy of 1%.

2.3.3. Electrical Resistivity Test. This paper takes KMP-cured zinc-contaminated red clay as the research object. The curing age is set at 1 d, 7 d, 14 d, and 28 d, and unconfined compressive strength-resistivity synchronous dynamic test is carried out. The resistivity test is carried out using the VC4091C LCR precision digital bridge, the effective range is 0.0001 \( \Omega \)-99.999 M\( \Omega \), and the parameters are set as low-frequency and alternating current (AC). After referring to the literature, 50 Hz is used as the current frequency of contaminated soil resistivity measurement. According to Ohm’s law, the resistance \( R \) measured in the test is converted into resistivity by the following equation:

\[
\rho = R \frac{S}{L}.
\]

In the formula, \( \rho \) is the resistivity of the specimen (\( \Omega \cdot m \)); \( R \) is the measured resistance of the soil sample (\( \Omega \)); \( S \) is the cross-sectional area of the soil specimen (m²); \( L \) is the distance between the electrode sheets (m).

All experiments were carried out in three groups of parallel experiments, and the test results were averaged.

| Table 2: The design schemes for the curing experiments. |
|-----------------|-----------------|-----------------|
| Concentration of KMP (%) | Unconfined compressive strength (kPa) |
| 0.1% | 0.5% | 1% |
| 4% | Zn0.1K4 | Zn0.5K4 | Zn1K4 |
| 6% | Zn0.1K6 | Zn0.5K6 | Zn1K6 |
| 10% | Zn0.1K10 | Zn0.5K10 | Zn1K10 |

Figure 1: Relationship between KMP content and strength at different \( \text{Zn}^{2+} \) concentrations.

Figure 2: The stress-strain curve of different KMP contents.
3. Results and Discussion

3.1. Analysis of Unconfined Compressive Strength. The effects of different initial heavy metal concentrations and KMP content on the unconfined compressive strength of the specimens at the curing age of 1 d are shown in Figure 1. It can be seen from the figure that for the samples with different KMP contents, the unconfined compressive strength increases correspondingly with the increase of the contents of the curing agent, and the increase of Zn$^{2+}$ concentration weakens the unconfined compressive strength of red clay. When the Zn$^{2+}$ concentration is 0.5%, the unconfined compressive strength increases slightly with the increase of KMP content. And the strength is similar when the Zn$^{2+}$ concentration is 0.05% and 0.1%, indicating that a small amount of Zn$^{2+}$ content has limited influence on red clay, so the Zn$^{2+}$ concentration of 0.1% was selected as the representative of low pollution concentration in the subsequent experiments.

Figure 2 shows the stress-strain curves of samples with different KMP contents when the curing time is 28 d and the Zn$^{2+}$ concentration is 1%. After the curing time increased to 28 d, the strength of the sample increased slowly. With the decrease of KMP content, the unconfined compressive strength curve changes from a typical strain-softening type to a weak strain-softening type. The main reasons are as follows: after the soil is polluted by Zn$^{2+}$, Zn$^{2+}$ and H$^+$ are generated with the large hydrolysis of Zn-containing pollutants, which will undergo complex chemical corrosion reactions with the mineral components in the red clay. Therefore, the weakening of the cementation between...
soil particles will destroy water-stable aggregates and change the soil structure. With the increase of pores, the contact area between soil particles becomes smaller, and the connection strength decreases, which weakens the stability of the soil and eventually leads to a weakening of the unconfined compressive strength. The fixation of Zn$^{2+}$ by KMP is mainly through the direct adsorption of Zn$^{2+}$ by ion exchange, and the cation adsorption can reduce the movement of Zn$^{2+}$ in the soil due to the increase of H$_2$PO$_4^-$. After exchange, and the cation adsorption can reduce the movement of Zn$^{2+}$ in the soil due to the increase of H$_2$PO$_4^-$. After adding KMP, the strength of polluted red clay can be enhanced to a certain extent.

3.2. Analysis of pH Value. Figure 3 shows the histogram of KMP content and the measured pH value at different Zn$^{2+}$ concentrations. It can be seen that the pH of KMP-cured zinc-contaminated red clay shows a decreasing trend with the increase of Zn$^{2+}$ concentration. In the case of the same Zn$^{2+}$ concentration, with the increase of KMP content, the pH value generally shows a rising law.

The pH value of soil will affect the composition ions of soil pore fluid and further affect its chemical reaction. The pH value of KMP-solidified contaminated soil is relatively concentrated, ranging from 8.5 to 10.5. The acidic environment is favorable for the reaction between Zn$^{2+}$ and KMP to generate metal phosphates with low solubility, which is beneficial to the leaching stability of Zn$^{2+}$. The high concentration of heavy metals has little inhibition of KMP hydration reaction, and the hydration products of KMP and Zn-containing compounds are less affected by the environment. To sum up, compared with the traditional curing agent, the pH value of the KMP-cured polluted soil changes less with the initial heavy metal concentration and the amount of curing agent. For standard curing, the pH value of KMP-solidified polluted soil changes stably, which effectively avoids the secondary damage caused by acid and alkali pollution to the environment.

3.3. Analysis of Resistivity. When the concentration of Zn$^{2+}$ is 0.5%, the effect of KMP content and curing age on the initial resistivity is shown in Figure 4. With the increase of curing age, the initial resistivity gradually increases. The initial resistivity increases with the increase of KMP content. Besides, the KMP content has a good linear relationship with the initial resistivity at different curing ages. With the increase of curing age, Zn$^{2+}$ ions will be fixed through surface adsorption and complexation, and then, from insoluble material precipitation, the amount of free Zn$^{2+}$ in the soil decreases. In addition, with the complex chemical reaction occurring in the curing process, the free Fe$^{2+}$, Fe$^{3+}$, Al$^{3+}$ liquid in the pore fluid of red clay decreases, the cementation between soil particles increases, the gap between soil particles decreases, and the contact area increases, which weakens the conductivity of soil and increases the resistivity.

When the curing age is 1 d, the influence of different Zn$^{2+}$ concentrations and KMP content on the initial resistivity is shown in Figure 5. The initial resistivity decreases with the increase of metal ion concentration. As widely known, red clay is a special kind of soil and its engineering characteristics are inseparable from the cementation of soil particles. With the increase of Zn$^{2+}$ concentration, the acidity of the soil increases, which will gradually dissolve the free oxides in the soil and weakens the cementation between soil particles. The repulsion will be reduced to accumulate small particles, and the pores between soil particles will increase, the pore channels of the soil will also become larger, and the conductivity of the pore liquid will also become larger, and the conductivity of the pore liquid will increase, resulting in a decrease in the resistivity.

3.4. Relationship between Unconfined Compressive Strength and Resistivity. Unconfined compressive strength is one of the most important parameters for evaluating soil solidification effect. Resistivity is an inherent physical property of soil. Taking 14 days of curing as an example, when the content of
KMP is 6%, the synchronous change curves of stress-strain-resistivity of red clay with Zn$^{2+}$ pollution concentration of 0.5% and 0.1% are shown in Figure 6 ($N$ represents the Zn$^{2+}$ content). The unconfined compressive strength of KMP-cured zinc-contaminated red clay corresponds to a relatively small strain, within 2%. With the increase of Zn$^{2+}$ concentration, the unconfined compressive strength decreases gradually, and the resistivity also decreases with the increase of metal ion concentration.

After curing for 28 days, the Zn$^{2+}$ pollution concentration is 0.1%, and the stress-strain-resistivity synchronous change curve of red clay under different KMP contents is shown in Figure 7 ($K$ represents the KMP content). It can be seen from the stress-strain curve that under the condition of low pollution concentration when the KMP content is increased to 10%, the unconfined compressive strength is greatly improved. The axial strain corresponding to the maximum stress of Zn$^{2+}$-contaminated red clay after KMP curing is small, within 2%. With the increase of KMP content, the peak point of stress shifts gradually to the right, which means the axial strain at failure becomes smaller. It can be seen from the resistivity-strain curve that the resistivity decreases rapidly with the increase of strain and then increases gently after reaching the minimum value.

From the stress-strain-resistivity synchronous change curve, it can be inferred that the stress and resistivity have opposite trends with the increase of strain. The minimum value of resistivity corresponds to the peak value of uniaxial compression. When the stress-strain curve reaches the peak, the resistivity-strain curve reaches the bottom. The stress

Figure 7: The synchronous variation trend of stress-strain-resistivity under different KMP content.
increases rapidly with the increase of strain, and the corresponding resistivity drops rapidly before the valley bottom and then flattens out. Before the destruction strain, the rate of increase in stress is roughly the same as the rate of decrease in resistivity with increasing strain.

The main internal mechanism of this phenomenon is that the current propagates mainly through three lines in soil: soil particle gap, pore-liquid gap, and soil-water gap. In the initial stage of the unconfined compressive strength test, the structure of the soil has not been destroyed. With the increase of stress, the pore space of soil is compressed and reduced, the contact area of soil increases, which enhanced the conductivity of soil. And in the process of compaction, as the air is expelled, the thickness of the water film becomes thinner. The large pores in the agglomerate are compressed, and the porosity is reduced, which enhances the connectivity between the pores, thereby greatly improving the conductivity of the soil. Therefore, the resistivity decreases rapidly with the increase of strain in the initial stage. When the stress reaches the peak point, the cracks of the soil sample become more and more, and the failure surface becomes larger and larger. At this time, the conductive path of some soil particles is blocked, and the conductivity is weakened. Therefore, after the stress peak point, the resistivity increases with the increase of strain. It can be seen that the synchronous resistivity change rule can accurately reflect the corresponding strength change process of red clay under load, which can promote the application of resistivity method in the study of mechanical strength characteristics of red clay.

4. Conclusions

In this paper, unconfined compressive strength test, pH test, and resistivity test were carried out for KMP-cured zinc-contaminated red clay, and the following conclusions can be drawn:

(1) The unconfined compressive strength of red clay is significantly weakened by the concentration of Zn$^{2+}$. The increase of KMP content can effectively improve the mechanical properties of red clay. The stress–strain curve shows a strain-softerning type, and with the increase of curing agent content, the peak point corresponding to the axial stress “shifts to the left” gradually.

(2) KMP can effectively control the pH value of zinc ion-contaminated red clay. The soil pH value under different Zn$^{2+}$ concentrations is controlled within 10.5. Compared with the highly alkaline environment treated with a traditional curing agent, it is environmentally friendly.

(3) There is a good linear relationship between the initial resistivity and different variables such as Zn$^{2+}$ concentration, KMP content, and curing time. Using the resistivity method, a rapid and quantitative non-destructive evaluation of Zn$^{2+}$-contaminated red clay curing sites can be achieved.

(4) The stress-strain-resistivity synchronous change curve of under different Zn$^{2+}$ concentrations and curing agent content shows good agreement. This correlated synchronous change relationship can promote the application of resistivity method in the study of the strength characteristics of heavy metal contaminated red clay.

Data Availability

The data used to support the findings of this study are included in the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References


