International Journal of Energy
ISSN: 2957-9473 | Vol. 4, No. 2, 2024

Characterization of Red Mud-based Curing Agent for Curing High Concentration Copper Contaminated Soil

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Abstract: In order to investigate the characteristics of RCP (red mud: calcium carbide slag: cement = 3:1:1) curing agent for curing soil with high concentration of copper contamination, this paper carried out the unconfined compressive strength test, toxicity leaching test, electrical resistivity test, and scanning electron microscopy test on RCP specimens with different age of maintenance, different curing agent dosages and different initial heavy metal contamination concentrations to investigate and analyze the Unconfined compressive strength characteristics, heavy metal ion leaching concentration characteristics and resistivity characteristics of RCP cured soil under different variables.It was found that the unconfined compressive strength and resistivity of RCP cured soil increased with the increase of maintenance age and curing agent dosing, while the strength and resistivity of cured soil decreased when the initial heavy metal contamination concentration increased. The heavy metal ion leaching concentration of RCP cured soil decreased with the increase of maintenance age and curing agent dosage, while the heavy metal ion solidification rate of cured soil decreased when the initial heavy metal pollution concentration increased.By observing and analyzing the swept electron microscope images of RCP specimens maintained for 28 days, the presence of Calcovanite, hydrated calcium silicate and hydrated calcium silica-aluminate can be observed, and these hydration reaction products enhance the strength of the cured soil, as well as displace and adsorb heavy metal ions in the contaminated soil, which have a better curing effect on the heavy metal ions.

Keywords: Red Mud; Curing; Heavy Metals; Unconfined Compressive Strength; Toxic Leaching Concentration; Resistivity; Microanalysis.

1. Introduction

As industrialization continues to move forward, the problem of soil pollution is becoming increasingly serious, with heavy metals leading the way, which has posed a great threat to ecosystems and human health [1]. Curing/ stabilization technology is an economically feasible and widely applied method to deal with the problem of heavy metal contaminated sites, and the contaminated soil after curing treatment will have a greater increase in strength and solidification rate for heavy metals. At present, common silicate cement is a widely used curing agent material, but the production of cement consumes a lot of energy and emits greenhouse gases, which is not friendly to the environment. Therefore, many scholars have begun to study the use of industrial solid waste as a substitute for traditional curing agents such as cement.

Both red mud and calcium carbide slag are common industrial solid wastes, red mud is the waste residue produced during the production process of alumina industry and calcium carbide slag is the solid waste residue produced during the production of acetylene from calcium carbide. Red mud and calcium carbide slag are produced in high volumes each year and are mainly disposed of in open piles, which can pollute the soil, atmosphere and groundwater [2]. Therefore, combining industrial solid wastes such as red mud and calcium carbide slag with solidification/stabilization is of great significance for the protection of the environment and the sustainable use of resources.

In recent years many scholars have conducted research on the reuse of industrial solid wastes such as red mud and calcium carbide slag.Wang et al. found that the admixture of 5% red mud to polluted soils could increase plant yield and reduce the proportion of heavy metal ion exchangeable state [3]. Yang Huizhu et al. prepared red mud based material and used it to solidify lead contaminated soil and found that the red mud based material could solidify different concentrations of lead in the soil, which resulted in a significant decrease in the proportion of lead in the exchangeable state in the soil [4].F. Kilinckale et al. used red mud with fly ash and cement as a curing agent, and found that the leaching concentration of metal ions, such as copper and lead, was much lower than the specified harmlessness standard values [5].Y. K. Kim used red mud and phosphogypsum to solidify/stabilize seabed sediments containing four heavy metals, Pb, Cd, Zn and Ni, and the concentrations of the four metal ions decreased significantly after solidification [6]. Chen Yonggui et al. used calcium carbide slag and metakaolin to prepare geopolymer to solidify/stabilize copper-contaminated soil, and analyzed the influence of the dosage on the leaching characteristics, and found that when the dosage of calcium carbide slag was 2% and the dosage of metakaolin was 5%, the geopolymer was the most effective in solidifying the copper-contaminated soil [7].

In this study, the characteristics of RCP (red mud: calcium carbide slag: cement = 3:1:1) cured soil with high concentration of copper contamination were investigated, and the unconfined compressive strength characteristics, heavy metal ion leaching concentration characteristics and electrical resistivity characteristics of RCP cured soil were investigated in terms of different curing agent admixture, different heavy metal contamination concentration and different age of curing, respectively.

2. Materials and Methods

2.1. Materials

The basic physical indexes of the soil samples used in this test are shown in Table 1, and the particle size distribution of the soil samples is shown in Figure 1. The soil samples were crushed after natural air-drying, passed through 2mm sieve, measured its air-drying moisture content and then sealed and stored in bags, and kept as the test soil.

The curing materials for this experiment included red mud (RM), calcium carbide slag (CS) and cement (PC). The red mud used in this experiment was taken from the Bayer method red mud produced by an aluminum company in Shaanxi Province, the calcium carbide slag was taken from a chemical plant in Hebei Province, and the cement was ordinary silicate cement. The heavy metal pollution source used in this test is copper nitrate trihydrate($Cu(NO3)_2 \cdot 3H2O$).

Table 1. Basic Physical Indicators of Test Soil

Natural moisture content/%	Liquid limit/%	Plastic limit/%	Plasticity index	Maximum dry density /(g/cm^3)	Optimal Water content/%
22.83	37.94	17.86	20.08	1.69	16.53

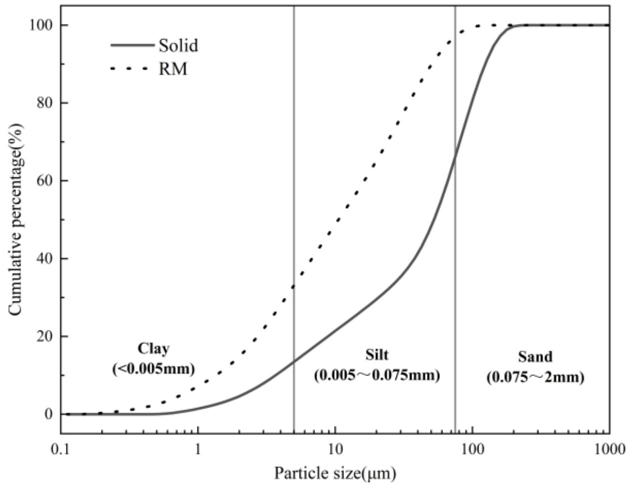


Figure 1. Particle size grading curves of test materials

2.2. Testing Methods

Based on previous studies, RCP (red mud: calcium carbide slag: cement = 3:1:1) was selected as the curing agent program for this experiment, and the properties (unconfined compressive strength, heavy metal ion leaching concentration, electrical resistivity, and microstructure) of RCP specimens at different curing agent dosages and at different concentrations of heavy metal contamination were investigated, respectively. In order to study the characteristics of cured soil under different curing agent dosage, the heavy metal contamination concentration of the specimens was designed to be 5000 mg/kg, and the curing agent dosage was designed to be 5%, 7.5%, 10%, 12.5%, and 15%. In order to study the properties of cured soil with different initial heavy metal contamination concentrations, the curing agent dosage was designed to be 10%, and the initial heavy metal contamination concentrations were designed to be 2500mg/kg, 5000mg/kg, 7500mg/kg, and 10000mg/kg.The curing ages of the specimens were designed to be 7 days, 14 days, and 28 days.

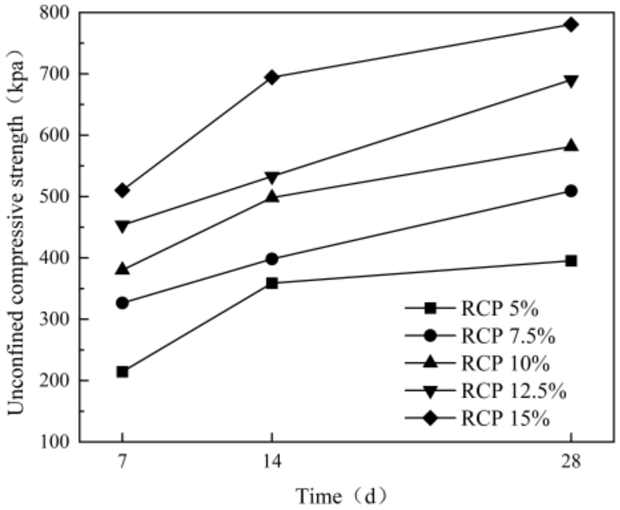
Cylindrical specimens with a diameter of 39.1 mm and a height of 80 mm were prepared according to the design values, and the specimens were placed in a standard curing box and cured until the corresponding age. The cured specimens were subjected to unconfined compressive strength test, toxicity leaching test, resistivity test and scanning electron microscope test.

3. Results and Discussion

3.1. Unconfined Compressive Strength

Fig. 2 (a)shows the unconfined compressive strength at different RCP dosages, where the heavy metal copper pollution concentration is 5000 mg/kg, and the unconfined compressive strength value in the figure is the average of three parallel samples. As can be seen from the figure, the unconfined compressive strength of RCP specimens increased with the increase of the age of maintenance, and the strength of RCP specimens was gradually enhanced with the increase of the curing agent doping. 5 kinds of curing agent doping, when the curing agent doping of 5%, the unconfined compressive strength of RCP specimens was the lowest, and the unconfined compressive strengths of the 7-day and 28-day were 214.53 kpa and 395.43 kpa, respectively. When the dosage of curing agent is 15%, the unconfined compressive strength of RCP specimens reaches the highest value, and the unconfined compressive strengths of 7 days and 28 days are 510.21kpa and 780.63kpa, respectively.The product of hydration reaction of curing soil, calcium hydrated silicate (C-S-H), is generated in large quantities, which fills up the structure gradually to make the structure of the soil body more dense, and at the same time, it has a bonding effect on the particles, so that the strength of the specimen is improved by the dosage of curing agent. The strength of the specimen is thus improved. At the same time, the alumina provided by the red mud in the curing agent reacts with calcium hydroxide and sulfate to produce calomel, which also plays a role in improving the strength of the soil body. The hydration reaction within the soil body proceeds more thoroughly with increasing age of curing, so the strength is enhanced with increasing age of curing. When the amount of curing agent in the specimen was increased, the products of the hydration reaction also increased, which had a positive contribution to the strength.

Figure 2 (b) shows the unconfined compressive strength of RCP specimens under different heavy metal pollution concentrations, in which the curing agent doping is 10%, from the figure it can be seen that with the increase of the initial heavy metal pollution concentration, the curing effect of the RCP specimens decreases, and the unconfined compressive strength of the specimens decreases. When the heavy metal copper pollution concentration is 2500mg/kg, the 7-day and 28-day unconfined compressive strength of the specimen is 512.8kpa and 968.31kpa, respectively; when the heavy metal pollution concentration is increased to 10000mg/kg, the 7-day and 28-day unconfined compressive strength of the specimen is 268.92kpa and 415.91kpa, respectively.When the heavy metal pollution concentration is high, it will inhibit the hydration reaction, the high concentration of heavy metal ions will lead to the generation of a large number of insoluble precipitates, these insoluble precipitates will be wrapped up in the soil particles, thus preventing the hydration reaction from proceeding further, and the generation of hydration products will be reduced, which will ultimately lead to the reduction of the strength.



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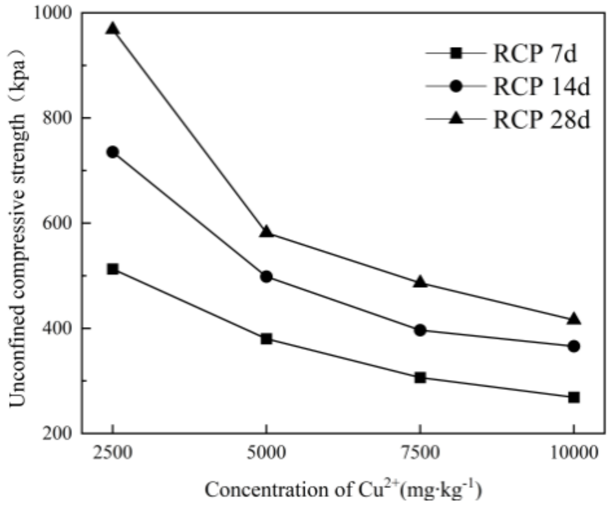
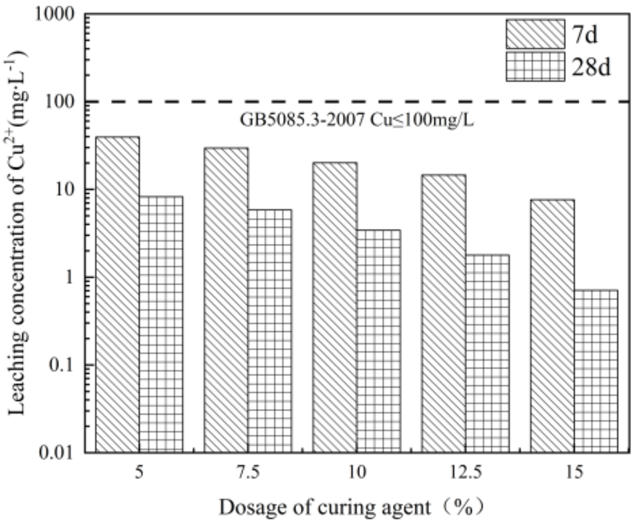


(b)

Figure 2. Unconfined compressive strength of RCP cured soils

3.2. Leaching Concentration of Heavy Metal Ions

Figure 3 (a) shows the copper ion leaching concentration under different RCP doping, in which the heavy metal copper contamination concentration was 5000mg/kg, as can be seen from the figure, the ion leaching concentration of the RCP specimens decreased with the increase of the age of the curing period, and with the increase of the curing agent doping, the ion leaching concentration of the RCP specimens also decreased gradually.Among the five curing agent doping, when the curing agent doping was 5%, the RCP specimens had the Among the five curing agent dosages, when the curing agent dosage was 5%, the ion leaching concentration of RCP specimens was the highest, and the copper ion leaching concentrations at 7 days and 28 days were 39.51 mg/L and 8.25 mg/L, respectively, with a curing rate of 96.7% at 28 days; when the curing agent dosage was 15%, the ion leaching concentration of RCP specimens reached the lowest value, and the ion leaching concentrations at 7 days and 28 days were 7.63 mg/L and 0.71 mg/L, respectively, with a curing rate of 99.7% at 28 days. curing rate was 99.7%. The hydration reaction produced a large amount of hydrated calcium silicate and hydrated calcium silica-aluminate, and the calcium ions in these hydration products would participate in the competition reaction of heavy metal ions, resulting in the replacement of Cu^{2+} into the hydrated calcium silicate and hydrated calcium silica-aluminate, and the structure formed was more stable. In the product of hydration reaction, the cation in Calcovanadium stone can also be replaced with Cu^{2+}, and the heavy metal ions will be fixed in Calcovanadium stone to play a curing role. When the dosage of curing agent is increased, the hydration products such as calcium silicate hydrate, calcium silica-aluminate hydrate and calcium vanadate are also increased, which leads to more Cu^{2+} being replaced into these hydration products, and thus the curing rate is improved.



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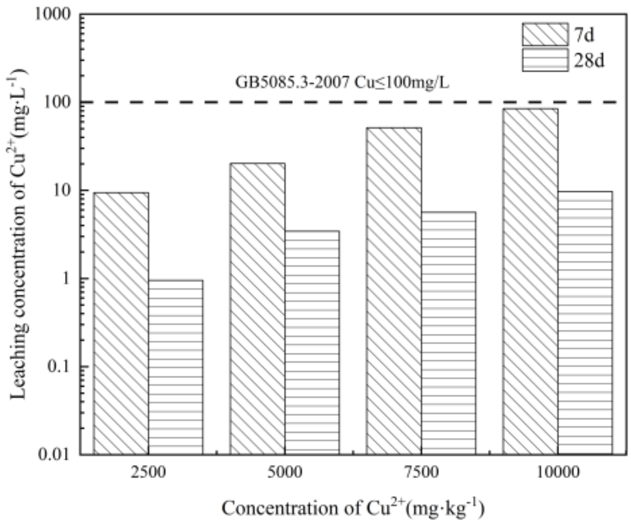


(b)

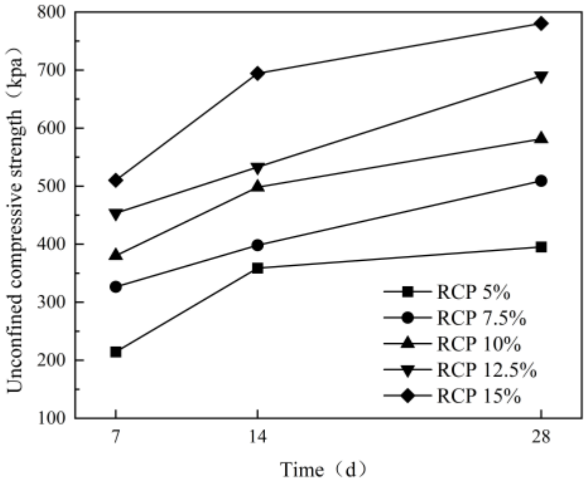
Figure 3. Leaching concentration of heavy metal ions from RCP solidified soil

Figure 3 (b) shows the copper ion leaching concentration of RCP specimens under different heavy metal pollution concentrations, where the curing agent doping is 10%, from which it can be seen that with the increase of the initial heavy metal pollution concentration, the curing effect of the RCP specimens decreases, and the copper ion leaching concentration of the specimens decreases. When the heavy metal copper pollution concentration was 2500mg/kg, the 7-day and 28-day copper ion leaching concentration of the specimen was 9.42mg/L and 0.95mg/L, respectively, and the curing rate of 28 days was 99.2%; when the heavy metal pollution concentration was increased to 10000mg/kg, the 7-day and 28-day unconfined compressive strength of the specimen was 84.56mg/L and 9.69mg/L, respectively. 9.69 mg/L, and the curing rate at 28 days was 98.1%. As the concentration of heavy metal pollution increases, it will inhibit the hydration reaction in the cured soil, which is not conducive to the generation of hydration products such as hydrated calcium silicate, so the curing rate of the soil specimen with high concentration of heavy metal pollution is lower compared with that of the soil specimen with low concentration of heavy metal pollution.

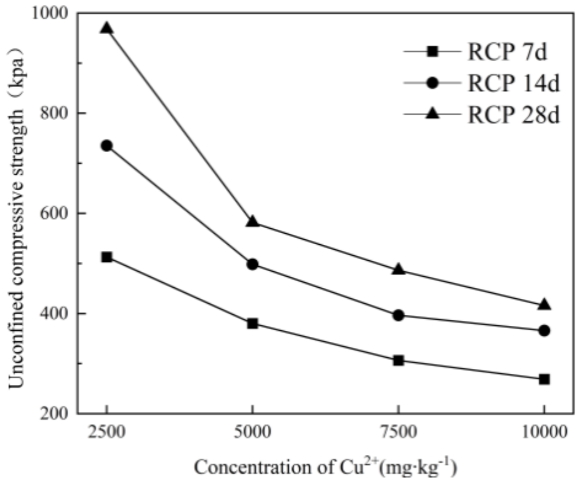
3.3. Resistivity

Figure 4 (a)shows the resistivity at different RCP doping levels, in which the heavy metal copper pollution concentration is 5000 mg/kg. It can be seen from the figure that the resistivity of RCP specimens increases with the increase of the age of the curing period, and with the increase of the curing agent doping level, the resistivity of RCP specimens is also gradually increased. among the five curing agent doping levels, the resistivity of RCP specimens is the lowest when the doping level is 5%, and the resistivities of 7 days and 28 days were 1.6531 Ω·m and 2.5613 Ω·m, respectively; when the amount of curing agent was 15%, the resistivity of the RCP specimens reached the highest value, and the unconfined compressive strengths at 7 days and 28 days were 3.9178 Ω·m and 5.2054 Ω·m, respectively. With the hydration reaction going on, the water in the pores of the soil body was being consumed continuously, and the electrical conductivity of the water pathway in the soil body was also reduced. Conductivity is also reduced, at the same time, the generation of a large number of hydration products will also lead to the filling of pores in the soil, the porosity decreases and the conductive path between the solids increases, which is macroscopically manifested as an increase in the electrical resistivity of the specimen. The increase of the maintenance age and the dosage of curing agent is conducive to the hydration reaction, so the resistivity of the specimen is also increased.

Figure 4 (b) shows the resistivity of RCP specimens at different heavy metal pollution concentrations, where the curing agent doping is 10%, from which it can be seen that with the increase of the initial heavy metal pollution concentration, the curing effect of the RCP specimens decreases and the resistivity of the specimens decreases. When the heavy metal copper pollution concentration is 2500mg/kg, the resistivity of 7 days and 28 days of the specimen is 5.6023Ω·m and 7.4012Ω·m, respectively; when the heavy metal pollution concentration is increased to 10000mg/kg, the resistivity of 7 days and 28 days of the specimen is 1.4089Ω·m and 1.7078Ω·m, respectively. high heavy metal pollution concentration has a hindering or delaying effect on hydration reaction. When the concentration of heavy metal ions is high, a large number of insoluble products are produced which are attached to the surface of soil particles and curing agent, thus hindering the rate and extent of hydration reaction, the porosity is high in comparison, and a large amount of electrically conductive Cu^{2+} which is not cured exists in the pore water, thus the electrical conductivity of the soil body is increased, and the electrical resistivity is decreased.



(a)



(b)

Figure 4. Resistivity of RCP cured soils

3.4. Scanning Electron Microscopy

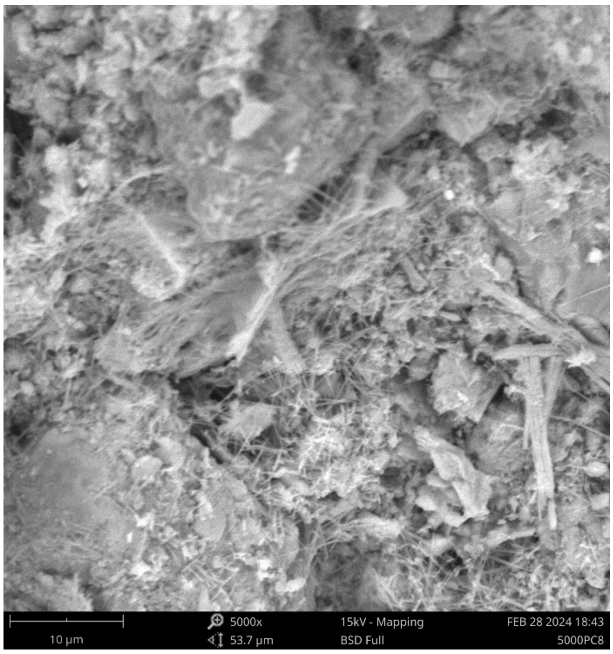


Figure 5. Micro-morphology of RCP cured soil

Figure 5 shows the microscopic morphology of the RCP specimen maintained for 28 days, the age of maintenance is 28 days, the pollution concentration of heavy metal copper is 5000mg/kg, and the magnification is 5000 times. From the magnified 5000 times electron microscope images, it can be seen that a large number of needle-like or columnar Calcovanadite exists, and a large number of hydrated calcium silicate and hydrated calcium silica-aluminate are filled in between particles, and these hydration products fill the pore spaces between soil particles, so that the soil forms a denser structure. The heavy metal ions in the contaminated soil were firmly fixed in these hydration products due to the substitution reaction, forming a stable structure and enhancing the curing effect of the soil, which was macroscopically manifested in the changes of unconfined compressive strength, heavy metal ion leaching concentration and electrical resistivity of the cured soil specimens.

4. Conclusion

(1) The unconfined compressive strength and electrical resistivity of RCP-cured soil increased with the increase of maintenance age and curing agent dosage, while the strength and electrical resistivity of cured soil decreased when the initial heavy metal contamination concentration increased.

(2) The heavy metal ion leaching concentration of RCP cured soil decreased with the increase of maintenance age and curing agent dosage, while the heavy metal ion curing rate of cured soil decreased when the initial heavy metal contamination concentration increased.

(3) The hydration products of RCP curing agent curing high concentration of copper contaminated soil are mainly calcium vanadate, hydrated calcium silicate and hydrated calcium silica-aluminate, and these hydration products enhance the strength of the cured soil body while also have the replacement and adsorption effects on the copper ions in the contaminated soil.

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