

Red Mud, Calcium Carbide Residue Respectively Solidify Lead-contaminated Granite Residual Soil Effect Comparison

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Abstract: *The purpose of this study is to investigate the effect of solidifying lead-contaminated granite residual soil with red mud and calcium carbide slag respectively, and to test the unconfined compressive strength, water stability and lead ion leaching concentration of the solidified soil. The solidification effects of red mud and calcium carbide slag were compared and analyzed in order to provide some ways and ideas for the remediation of heavy metal contaminated soil. In the study, we used different amounts of red mud and calcium carbide slag to solidify the granite residual soil contaminated by lead. With the progression of the curing period, the unconfined compressive strength of the stabilized soil was evaluated. The findings indicate that augmenting the quantity of the curing agent markedly enhances the mechanical robustness of the stabilized soil. Although the strengthening effects of red mud and calcium carbide slag are different in different content, both of them can achieve higher strength curing standard in a certain range. among them, the strengthening effect of calcium carbide slag on the strength of solidified soil is particularly significant. Through the water stability test, it is found that the calcium carbide slag solidified soil can still maintain good stability under the action of soaking, while the red mud solidified soil disintegrates under the same conditions, indicating that the solidification treatment of calcium carbide slag can effectively improve the water erosion resistance of the soil. In addition, we also measured the leaching concentration of lead ions in the solidified soil. The results show that the leaching concentration of lead ion decreases with the increase of curing agent content. Both red mud and calcium carbide slag show good performance in lead ion solidification, but red mud is more outstanding in reducing the leaching concentration of lead ion. To sum up, through the comparative analysis of the curing effect of red mud and calcium carbide slag on lead-contaminated granite residual soil, it is found that both can effectively improve the unconfined compressive strength of the solidified soil and significantly reduce the leaching concentration of lead ions. Calcium carbide slag performs better in water stability and red mud performs better in reducing the leaching concentration of lead ions. These findings can provide ideas for the comprehensive utilization of industrial wastes and provide practical guidance for the green remediation of heavy metal contaminated soils.*

Keywords: Industrial solid waste, Lead contaminated soil, Mechanical properties, Leaching toxicity.

1. Introduction

Investigations and studies have shown that the current situation of soil pollution in China is serious, and the total over-standard rate of soil is 16.1%. The main pollutants affecting the soil environmental quality of agricultural land are heavy metals, of which the over-standard rate of inorganic pollutant lead is 1.5% [1]. With the continuous improvement of human quality of life and industrial production level, excessive lead content in soil has become a key concern for environmental control.

Solidification/stabilization technology, as an economically feasible resource recovery method, is widely used in the treatment of heavy metal contaminated sites and solid waste landfills [2], and is an effective means to ensure the efficient remediation and safe reuse of heavy metal contaminated soil. Red mud is a solid waste generated during the production process of the aluminum oxide industry. It has the characteristics of strong alkalinity and high salinity, which can easily cause salinization of the surrounding soil and pollution of underground water sources [3]. Calcium carbide slag is a general industrial solid waste mainly composed of $\text{Ca}(\text{OH})_2$ produced during the hydrolysis of calcium carbide to obtain acetylene gas [4]. Granite residual soil, as a common soil type, is widely distributed in various regions of China [5]. Granite residual soil is widely distributed in some areas with serious heavy metal pollution. As we all know, the soil homogeneity of granite residual soil is poor, it is easy to disintegrate in the presence of water, and the invasion of lead

pollutants will further reduce the strength of the soil [6]. Red mud and calcium carbide slag themselves will cause potential pollution to the environment. The combination of waste red mud and calcium carbide slag with curing / stabilization technology is of great significance to the green and sustainable utilization of resources [7].

In recent years, many scholars at home and abroad have carried out related research on the resource reuse of red mud and calcium carbide slag. KILINCKALE F et al. [8] use red mud mixed with fly ash and cement as curing agent. The results show that the concentration of Cu, Pb and other metals after leaching is much lower than the harmless standard value that can be discharged. Lee S et al. [9] used red mud, limestone and blast furnace slag to solidify As, Cd, Pb and Zn contaminated soil. the results showed that the leaching content of As, Cd, Pb and Zn in the solidified contaminated soil decreased by 58%, 98%, 98% and 99%, respectively. Liu Xiaofeng et al. [10] prepared red mud modified biochar (RMBC) by co-pyrolysis to study the effects of RMBC on the physical and chemical properties, remediation effect and engineering properties of lead contaminated soil. The results showed that with the increase of RMBC content and repair time, the lower the leaching concentration of Pb^{2+} , the better the remediation effect of 7% RMBC on lead-contaminated soil. In addition, the addition of RMBC can increase the compactness of soil and improve the bearing capacity and impermeability of soil to a certain extent. These studies show that red mud plays an effective role in soil improvement and solidification of contaminated soil. A large number of studies have found that calcium carbide slag can also solidify soil. Li

Yuanyuan et al. [11] calcium carbide slag was used to activate slag to solidify lead contaminated soil and uncontaminated soil respectively. The findings revealed that, under identical curing durations and equivalent quantities of curing agent, the unconfined compressive strength of solidified uncontaminated soil surpassed that of solidified lead-contaminated soil, and the void ratio of solidified soil decreased significantly, and the precipitation of hydration products C-S-H, AFt and Pb (OH)₂ could be observed in microstructure. Jun M et al. [12] calcium carbide slag was used to improve the acid paddy soil polluted by cadmium. The study shows that calcium carbide slag can transform the acid soluble part of cadmium ion into a more stable part, and can effectively increase the pH value of acidic paddy soil. Dejun H et al [13] used calcium carbide slag to solidify / stabilize heavy metals in electrolytic manganese residue. The results showed that when the content of calcium carbide slag was 7%, the leaching concentration of heavy metals in electrolytic manganese residue was lower than the standard limit after treatment for 24 hours, and calcium carbide slag could reduce its corrosivity at the same time.

In this study, the strength and chemical properties of

lead-contaminated granite residual soil solidified / stabilized by red mud and calcium carbide slag were investigated through unconfined compressive strength test, water stability test and TCLP toxicity leaching test. At the same time, combined with the test data, the ratio of red mud and calcium carbide slag curing agent was further optimized to provide important parameters and theoretical basis for the practical application of red mud and calcium carbide slag solidification / stabilization of heavy metal contaminated soil.

2. Materials and Methods

2.1 Materials

2.1.1 Granite residual soil

The granite residual soil samples used in this experiment were taken from Futian District, Shenzhen City, Guangdong Province. The recovered granite residual soil is naturally air-dried and removed impurities such as construction waste, gravel and plant roots, and then the air-dried soil samples are sifted through 2mm and placed in a cool place. The basic physical indexes of the test soil are shown in Table 1.

Table 1: Basic physical index of soil for test.

Natural density $\rho(g/cm^3)$	Specific gravity G_s	Dry density $\rho_d(g/cm^3)$	Moisture content %	Void ratio e	Liquid limit %	Plastic limit %	Plasticity index I_p
1.89	2.73	1.53	23.68	0.78	47.58	27.58	20.0

2.1.2 Red mud

The red mud selected in this study is the red mud prepared by sintering method. The red mud prepared by sintering method is gray powder particles, which is air-dried and bagged after 2mm standard sieve. The main chemical composition and content of red mud are shown in Table 2.

2.1.3 Calcium carbide slag

The calcium carbide slag selected in this study was naturally air-dried to remove impurities, crushed and screened by 2mm, and bagged as a spare. The main chemical composition and content of calcium carbide slag are shown in Table 2.

Table 2: Main chemical composition of industrial solid waste.

Materials	Main chemical composition/%					
	CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	MgO
Red mud	28.46	26.85	10.30	1.12	9.02	0.99
Calcium carbide slag	64.52	3.05	1.15	0.25	—	—

2.1.4 Lead nitrate

In view of the high solubility of nitrate and little interference to the hydration reaction in the curing process [14], Pb (NO₃)₂ reagent was selected for indoor manual preparation of lead contaminated soil. Lead nitrate used in this experiment was purchased from Shenzhen Fulin Standard solution Laboratory.

2.2 Preparation of Lead Contaminated Soil

A certain amount of air-dried granite residual soil was placed on a porcelain plate, and the prepared Pb (NO₃)₂ solution was

evenly sprayed into the soil and stirred evenly, then transferred to a sealed bag, and the soil moisture content in the bag was kept constant, stored at room temperature for more than 24 hours, so that lead ions and solid mixture were fully integrated to achieve the maximum pollution effect. The content of lead ion in soil reaches 3000mg/kg, which is 1.2 times of the control value of the second type of construction land (GB 36600-2018) [15].

This experiment mainly studies the mechanical strength and curing effect of lead contaminated soil with different curing agent ratio and curing time [16]. The content of calcium carbide slag is 0%, 5% and 10% of the mass of soil sample, respectively. The curing time is 7 days, 14 days and 28 days respectively, the detailed test grouping is shown in Table 3. The letter C in the table represents the content of calcium carbide slag. The letter R represents the amount of red mud, and the following number is the percentage of the curing agent. For example, C5 indicates that the content of calcium carbide slag in the curing agent is 5% of the quality of the soil sample R10 means that the amount of red mud is 10% of the mass of the soil sample.

Table 3: Mix ratio of test sample

Serial number	Soil samples	Curing agent content (The curing time is 7d/14d/28d)
1	Lead contaminated soil	R0C0
2	Lead contaminated soil	R5
3	Lead contaminated soil	C5
4	Lead contaminated soil	R10
5	Lead contaminated soil	C10

2.3 Samples Preparation

According to the Test rules for Inorganic Binder stabilized

Materials in Highway Engineering (JTG E51-2009) [17], a light compaction test was carried out on a single contaminated soil with a lead ion content of 0.3%. The test results are shown in Figure 1. which shows that the maximum dry density of lead contaminated soil is $1.592\text{g}/\text{cm}^3$, and the corresponding optimal water content is 17.6%.

The soil sample, distilled water and curing agent needed for the sample are calculated and weighed according to the compaction test data, and after fully uniform stirring, the soil sample is divided into three layers into the mold to prepare the cylindrical sample with the size of $39.1\text{mm} \times 80\text{mm}$, which is maintained in the standard curing room. After the curing temperature is $20 \pm 2^\circ\text{C}$ and the relative humidity is 95%, after 1d~2d, take out the mold and keep it in the curing room until the design age of the test scheme.

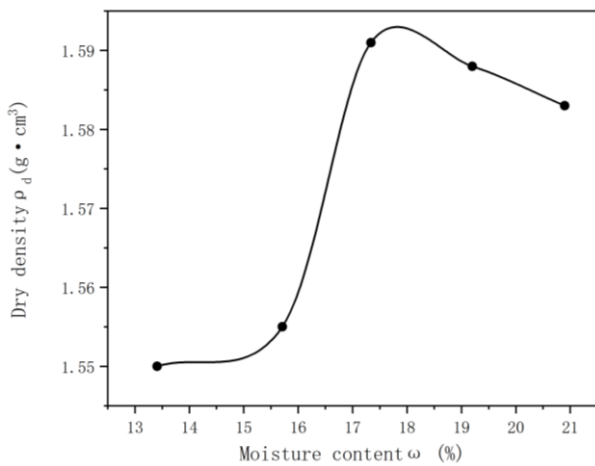


Figure 1: Compaction curve of lead contaminated soil.

2.4 Test Methods.

2.4.1 Unconfined compressive strength test

The bearing capacity of solidified soil is the key factor affecting the application of soil engineering. According to the Test Code of Inorganic Binder stabilized Materials for Highway Engineering (JTG E51-2009) [17], the unconfined compressive strength test of the sample was carried out by using YYW-2 strain-controlled unconfined pressure meter (as shown in Figure 2).



Figure 2: YYW- 2 strain-controlled unconfined manometer.

2.4.2 Water stability test

Water stability denotes the extent to which a material is influenced by water. Insufficient water stability can lead to water-induced deterioration, adversely impacting the mechanical characteristics and long-term durability of the soil. [18]. Therefore, in order to explore the water stability of lead contaminated soil solidified by red mud and calcium carbide slag, the water stability test of solidified soil was carried out.

According to the different curing methods, the samples were divided into immersion group and non-soaking group. The test process is as follows (taking the age of 14 days as an example): the unimmersed group refers to the sample after demoulding is packed into a sealed bag and then cured in a standard curing environment, which is maintained to the design age of 14 days, the sample is taken out and the mass m_1 of each sample is recorded, and then the strength test is carried out. The immersion group means that the sample after demoulding is cured for 13 days according to the non-soaking group, and the sample is taken out and put into water for one day. The immersion sample requires that there is permeable stone at the bottom of each sample, and the interval of each test piece should not be less than 50mm. After immersing in water for 1 day, the sample was taken out, the visible water was dried on the surface, the mass m_2 of each sample was recorded again, and then the strength of the sample was measured.

2.4.3 Toxicity leaching test

The toxicity leaching test (TCLP) was carried out according to the Chinese environmental protection standard "sulfuric acid-nitric acid method for toxic leaching of solid waste" (HJ/T 299-2007) [19]. The scientific compass company was commissioned to test each batch of leaching solution, and the test data were obtained and the leaching results were analyzed according to the Identification Standard of leaching toxicity of Hazardous waste (GB5085.3-2007).

3. Results and Discussion

3.1 Experimental Results and Analysis of Strength of Solidified Soil

3.1.1 Variation of unconfined compressive strength of red mud solidified soil

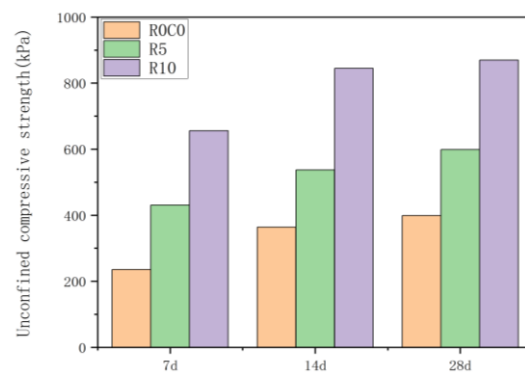


Figure 3: Relationship between unconfined compressive strength of solidified soil and red mud content and curing days.

The unconfined compressive strength test was used to analyze

the connection between red mud content and material properties, curing days and unconfined compressive strength was obtained, and the results are shown in Figure 3.

3.1.2 Variation of unconfined compressive strength of calcium carbide slag solidified soil

Through the unconfined compressive strength test, the relationship between the content of calcium carbide slag, curing days and unconfined compressive strength is obtained. the results are shown in Figure 4.

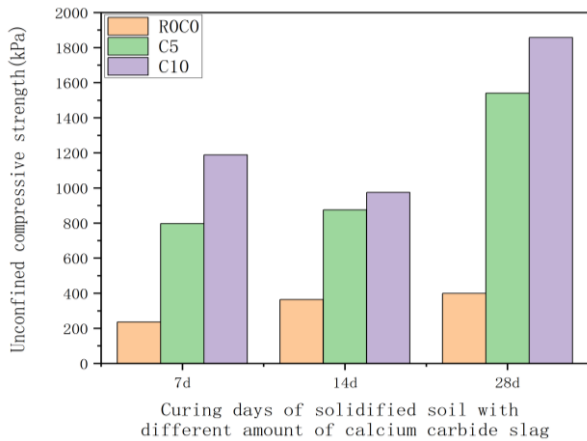


Figure 4: Relationship between unconfined compressive strength of solidified soil and content of calcium carbide slag and curing days.

3.1.3 Comparison of effects of red mud and calcium carbide slag on unconfined compressive strength of lead contaminated soil

As shown in Figure 3 and Figure 4, the unconfined compressive strength of solidified soil increases with the increase of curing age. Specifically, when the red mud solidified soil is cured for 28 days, the unconfined compressive strength of ROC0, R5 and R10 is 399.2kPa, 598.8kPa and 870.3 kPa respectively, while when the calcium carbide slag solidified soil is cured for 28 days, the unconfined compressive strength of ROC0, C5 and C10 is 399.2kPa, 1540.1kPa and 1840.0kPa respectively. It can be seen that the addition of red mud and calcium carbide slag can enhance the strength development of lead contaminated soil. for lead contaminated soil under the action of the same curing agent, the strength of solidified soil increases with the increase of curing agent addition. the results show that the addition of curing agent has an effect on the internal hydration reaction of solidified soil and optimizes the strength development of solidified soil. It can be seen from Table 4 that under the same curing time, such as 28 days, the unconfined compressive strength of 5% and 10% calcium carbide slag solidified soil is 2.6 times and 2.1 times higher than that of the same amount of red mud solidified soil. it is proved that calcium carbide slag has a better strengthening effect on the strength development of lead contaminated soil than red mud.

Table 4: Strengthening effect of red mud and calcium carbide slag on unconfined compressive strength of solidified soil

Curing agent	Strength ratio		
	7d	14d	28d
C5/R5	2.1	1.6	2.6
C10/R10	1.8	1.2	2.1

3.1.4 Water stability of solidified soil

Through the water stability test, the compressive strength of the immersion group is shown in Figure 5, and the softening coefficient η and mass change Δ_m are shown in Table 5. Among them, $\Delta_m = m_2 - m_1$ and softening coefficient η are the ratio of the unconfined compressive strength of the solidified soil in the immersion group to that in the unimmersed group [20].

Table 5: Water stability of solidified soil with different contents at different ages.

Mixing amount	Quality change Δ_m/g			Softening coefficient η		
	7d	14d	28d	7d	14d	28d
ROC0	—	—	—	—	—	—
R5	—	—	—	—	—	—
C5	10.80	10.63	10.58	70.76%	79.58%	83.34%
R10	—	—	—	—	—	—
C10	8.54	8.10	7.95	69.16%	71.75%	73.82%

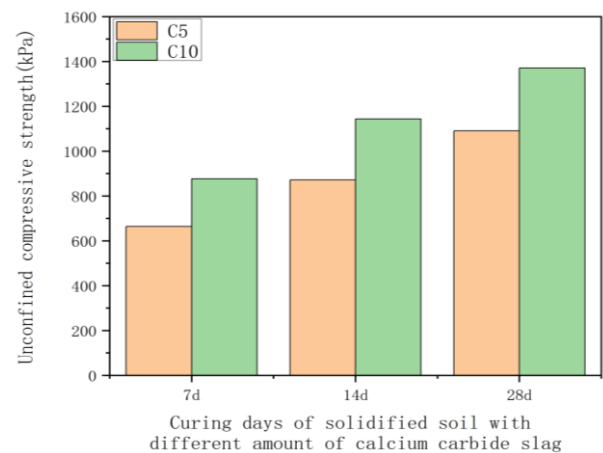


Figure 5: Relationship between unconfined compressive strength and content of calcium carbide slag and curing days in immersion group.

As can be seen from Table 5 and Figure 5, (1) only the unconfined compressive strength test was carried out on the solidified lead contaminated soil with calcium carbide slag as curing agent, this is because the samples ROC0, R5 and R10 disintegrated after soaking for 24 hours, and the unconfined compressive strength test could not be carried out, while the samples C5 and C10 of lead contaminated soil solidified with calcium carbide slag did not crack or defect. The softening coefficient of solidified lead contaminated soil at different ages is basically maintained at more than 70%, and the quality change of solidified soil is between 8 and 11, which proves that the water stability of lead contaminated soil solidified with calcium carbide slag is good. (2) At identical curing ages, the sample's softening coefficient declines as calcium carbide slag content rises, while the extent of quality change diminishes with higher slag content. The reason may be that with the increase of the content of calcium carbide slag, the content of lead ion decreases, and the blocking effect of lead ion on hydration reaction decreases, which makes the soil structure become compact, resulting in the decrease of soil water absorption and the change of sample quality. (3) When the content of calcium carbide slag is constant, the hydration reaction progresses more fully, leading to enhanced structural integrity and reduced porosity in the sample. This results in an increased softening coefficient, reflecting improved resistance to water-induced weakening. Simultaneously, the reduced quality change suggests greater stability and

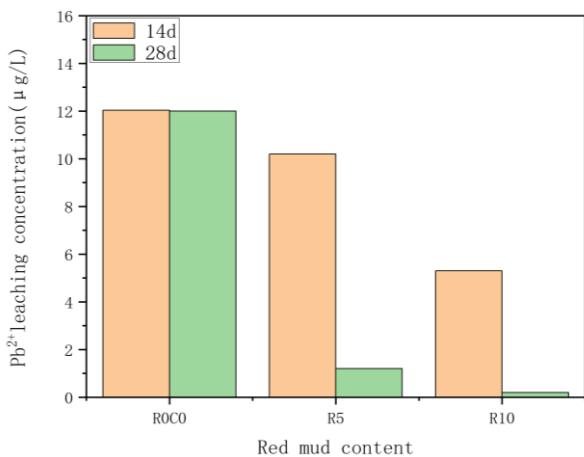
minimized material degradation over time. This phenomenon likely stems from the gradual formation of a denser and more cohesive matrix as the curing process advances, the hydration reaction in the soil is more sufficient, which makes the soil structure become a dense whole, and during the immersion period, the soil absorbs less water and reduces the mass change. at the same time, the free water in the soil decreases, the destructive effect of water on the internal structure of the soil decreases, and the softening coefficient of the sample increases.

To sum up, the red mud solidified lead contaminated soil does not have good water stability, and the sample of calcium carbide slag solidified lead contaminated soil has good water stability. The water stability of solidified soil improves with higher calcium carbide slag content and longer curing periods.

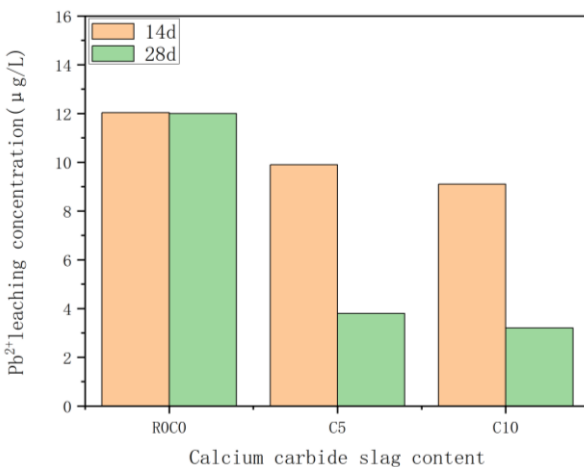
3.1.5 Study on leaching toxicity of solidified soil

Table 6: Lead ion leaching concentration of solidified soil.

Curing agent	Curing age	
	14d	28d
ROCO	12.031	12
R5	10.2	1.2
C5	9.9	3.8
R10	5.3	0.2
C10	9.6	3.2



(a) lead ion leaching concentration of solidified soil with different red mud content



(b) lead ion leaching concentration of solidified soil with different calcium carbide slag content

Figure 6: Relationship between lead ion leaching concentration and curing agent content and curing days.

It can be seen from Figure 6 that the leaching concentration of

lead ion decreases gradually with the increase of the amount of curing agent; compared with the untreated lead contaminated soil, the leaching concentration of lead ion decreases to a lower level with the increase of curing age. However, compared with Figure 6 (a) and (b), it can be seen that under the same conditions, red mud is more prominent in reducing the leaching concentration of lead ions. This is because red mud itself is rich in iron, aluminum, silicon and other elements, which can combine with Pb^{2+} to form silicon-aluminum compounds or iron-aluminum oxides, thus forming stable insoluble precipitates in biochar or soil [10]. And red mud has the functions of surface adsorption, precipitation and lattice fixation [21]. In addition, the hydration of red mud not only increases the pH of solidified soil, but also provides alkaline conditions for lead ion curing. Wei Jianhong et al. [22] studied the effect of red mud on the distribution of cadmium in soil. It was found that red mud particles increased the pH value of soil, changed the physical and chemical properties of soil, and increased the adsorption of cations to some extent. It can be seen from Figure 6 (a) that when the curing agent is red mud, the lead leaching concentration of solidified soil varies greatly with the increase of curing age, the lead ion concentration in the early stage is higher, the hydration reaction is seriously and insufficiently inhibited, and the hydration product formation is low [23]. The curing effect on Pb^{2+} is not strong enough, so the leaching concentration is higher.

3.2 Conclusion

In this study, through the comparative analysis of the curing effect of red mud and calcium carbide slag on lead-contaminated granite residual soil, the preliminary conclusions are as follows:

The unconfined compressive strength of solidified soil exhibits a positive correlation with both curing age and curing agent content. Notably, under identical conditions, calcium carbide slag demonstrates a more pronounced impact on enhancing soil strength compared to red mud.

The red mud solidified soil disintegrates after soaking, and the calcium carbide slag solidified soil can still maintain good stability under the action of soaking. Calcium carbide slag can effectively improve the water erosion resistance of the soil, and it increases with the increase of curing time and content.

With the increase of the amount of curing agent, the leaching concentration of lead ion decreased gradually. Both red mud and calcium carbide slag show good performance in lead ion curing, but red mud is more prominent in reducing the leaching concentration of lead ions.

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