A Comparative Study of Cement-Bentonite and Cement-Based Remediation of Lead-Contaminated Soils

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Abstract: The mixture of bentonite and cement at a mass ratio of 2:1 (recorded as BC) was used as solidifying agent to repair lead contaminated soil, and traditional cement (PC) was used as contrast solidifying agent. The comparative test results show that the soil restoration and maintenance period reach 7 days and 28 days respectively. Compared with PC solidified soil, the pH and EC value of BC solidified soil is lower, and the pH value and EC value of 4% and 8% BC-solidified soil meet the interval value needed for vegetation growth. The dissolution of heavy metals in BC-solidified soil and PC-solidified soil decreases with the increase of the content of solidifying agent. At the same content, the dissolution of heavy metals in BC-solidified soil is lower, which indicates that the mixed material (bentonite + cement) has better effect on the fixation of heavy metals. The unconfined compressive strength of BC-solidified soil and PC-solidified soil increases with the increase of the content of solidifying agent, but compared with PC-solidified soil, the unconfined compressive strength of BC-solidified soil decreases significantly. Lower unconfined compressive strength is beneficial to the secondary development and utilization of solidified soil. The above research results show that the mixed material of bentonite and cement can effectively fix the heavy metal lead in the soil, avoid the excessive strength of the soil, and consequently cause soil hardening and influence the re-development and utilization. The mixed material is a feasible and economical repair material.

1. Introduction

With the expansion of China's urban construction and the adjustment of industrial layout, many of the original sites of enterprises have become industrial pollution sites, seriously affecting the surrounding ecological environment. Therefore, effective measures must be taken to repair such polluted sites so as to achieve the function of re-development and utilization.

Solidification/stabilization method (S/S method) is a commonly used remediation technology for contaminated soil. Early S/S technology mostly used cement-based cementitious materials mixed with contaminated soil, through a series of physical and chemical reactions, to reduce heavy metal infiltration into groundwater.

Compared with other technologies, cement S/S technology has the following advantages [1-10]: cement materials and application technology are relatively mature, and the process of processing is simple and feasible; it can effectively deal with a variety of heavy metals, and can make most liquid waste react with cement chemically; the cement solidified soil formed has good long-term chemical
and physical stability, relatively good mechanical and structural properties, and relatively low permeability. But at the same time, cement solidifying agent also has some shortcomings, such as non-renewable, high energy consumption in production, excessive alkalinity of solidified soil, high strength and difficulty in secondary development, which limit the further development of cement into environmentally friendly repair materials. Therefore, it is necessary to develop curing materials with low carbon, environmental protection and easy development after repair.

In this study, bentonite and cement were mixed at a mass ratio of 2:1 to obtain a mixture (recorded as BC) as a solidifying agent for remediation of lead contaminated soil. The pH and EC values of PC solidified soil and BC solidified soil were tested by using cement (PC) as contrast solidifying agent. The environmental safety and strength characteristics of PC solidified soil and BC solidified soil after 28 days of standard maintenance were studied.

2. Testing materials and methods

2.1. Testing materials
The contaminated soil in this study was taken from a factory in Taizhou City, Jiangsu Province. The content of heavy metals in the soil was measured by X-ray fluorescence spectrometer (XRF). The soil taken from the site is sealed in a sealed bag and transported safely to the laboratory. The basic physical properties and test methods of the contaminated soil are shown in Table 1. The bentonite used in the experiment was purchased from a bentonite processing plant in Rizhao City, Shandong Province. The basic properties of the bentonite are shown in Table 2. The cement used in the test is 325 # composite Portland cement (PC). The bentonite and cement are mixed in proportion of 2:1 mass ratio, sealed in PE bottle, and the PE bottle is turned over and shaken for 24 hours to mix evenly. After 24 hours, the mixture material is taken out for reserve and recorded as BC. PC as a contrast solidifying agent, the content of BC and PC were set at 4%, 8% and 12% (as to the dry weight of contaminated soil).

The specific quality solidifying agent calculated according to the dosage will be mixed with the contaminated soil, which will be stirred by hand-held electric agitator at high speed for 10 minutes. Referring to the code CJ/T340-2011, about 127 g of solidified soil was pressed into a steel cylinder die with a diameter of 50 mm and a height of 50 mm by static compaction method, and its density was controlled to be about 1.30 g/cm³. Finally, the soil was demoulded and packed in a sealed bag. After 7 and 28 days of standard maintenance, 24 samples were prepared for each solidified soil, and four parallel samples were set for each group.

2.2. Testing methods
The tests for each sample in this study are listed in Table 3. The determination of pH value and EC value was carried out with reference to ASTM D4972-13 and CJ/T340-2011 respectively.

The toxicity leaching test (TCLP 1311) was used to measure the leaching of heavy metals from solidified soils. The leaching characteristics of solidified soils were analyzed by referring to the identification method of hazardous wastes specified in RCRA Code of the United States. The test method refers to the specifications. The curing age of the samples is 7 days and 28 days. Four parallel samples are set for each group and their average values are taken.

The unconfined compressive strength test is the same as that of conventional cement-soil test. The strength of solidified soil was tested for 7 and 28 days. The instrument used in the test was a conventional vertical loading device, and the axial strain rate was controlled at 1%/min (ASTM D2166-06). The samples were maintained in the standard curing room until the prescribed age. Four parallel samples were set in each group and their average values were taken.

| Table 1. Basic properties of the contaminated soil for testing |
|------------------|----------|------------------|
| index            | numerical value | test method |
| w (%)            | 24       | ASTM D2216-10   |
| proportion, Gs   | 2.679    | ASTM D5550-14   |
| WL (%)           | 34.1     | ASTM D4318-10   |
Table 2. Basic Properties of bentonite for testing

| Physical index                        | numerical value | test method   |
|---------------------------------------|-----------------|---------------|
| Classification of soil                | CH              | ASTM D 2487   |
| fine content / %                      | 100             | ASTM D 422    |
| Clay content / %                      | 44              | ASTM D 422    |
| proportion, Gs                        | 2.62            | ASTM D 854    |
| pH                                    | 8.45            | ASTM D 4972   |
| wL / %                                | 210.4           | ASTM D 4318   |
| SSA (m²/g)                            | 232             | EGME          |

3. Test results and analysis

3.1. Physicochemical properties of solidified soil

Fig. 1 shows the change of pH of contaminated soil before and after BC and PC remediation. Compared with contaminated soil before remediation, the pH of the two solidified soils at 7-day-old and 28-day-old increased uniformly. The pH value of BC and PC solidified soils increases with the increase of the content of solidifying agent, which is due to the alkaline materials of both BC and PC. Compared with 7-day-old soil, the pH of the two kinds of solidified soils at 28-day-old soil decreased. The main reason is that with the increase of curing age, more and more heavy metal lead is adsorbed by cement or bentonite, Hydrogen and oxygen radicals in solidified materials together with lead form insoluble alkali or CSH with precipitation property, and the concentration of hydroxide decreases continuously, so the pH decreases. However, according to relevant regulations, only when the pH value of solidified soil is within 5.5-8.3, can vegetation grow properly. So the cement solidified soil is too high to be suitable for vegetation growth; on the contrary, the pH value of BC solidified soil (7-day and 28-day age) with 4% and 8% content can be considered as planting soil in this range.

Fig. 2 shows the EC values of BC and PC solidified soils in 7 and 28 days. The EC value of contaminated soil is reduced to a certain extent by adding 4% BC mixture to the contaminated soil. The main reason is that BC mixture adsorbs electrolytes such as lead and calcium plasma in the soil. With the increase of BC content, the EC value increases slightly, which is due to the increasing cement content in BC. However, Compared with contaminated soil before remediation, the EC value
of cement-stabilized soils at different ages and dosages increased, ranging from 4 to 5 ms/cm. Under the same dosage, the EC value of 28-day-old cement-stabilized soils was less than that of 7-day-old soils, which was mainly caused by the continuous hydration of cement, and the electrolytes in soils were constantly fixed. Although the EC value of 28-day-old cement-solidified soil decreased, it was always higher than that of BC mixture-solidified soil, indicating that the addition of bentonite could effectively reduce the salinity and alkalinity of soil.

Figure 2 (a) Age: 7 days (b) Age: 28 days
Fig. 2. EC value of BC and PC solidified soil

3.2. Dissolution characteristics of solidified soil
Figure 3 (a) is the dissolution of [Pb] from contaminated soil before and after solidification and remediation by TCLP test. The curing period is 7 days and 28 days respectively. With the increase of curing age, the dissolution of [Pb] in the two kinds of solidified soils tends to decrease, which indicates that the combination of the two solidifying agents and contaminated soils continues to undergo physical and chemical reactions, and the fixation rate of [Pb] increases with the development of time. Compared with cement-solidified soil, the dissolution of [Pb] in BC-solidified soil is lower. According to the relevant regulations of USEPA and MEPC (2007), the dissolution concentration of [Pb] in soil should be less than 5 mg/L. The test results show that after 7 days of curing, the BC solidified soil with 12% content is close to the required requirements, while the cement solidified soil cannot meet the requirements. After 28 days of curing, the [Pb] of the two kinds of solidified soils decreased, and the dissolution of the BC solidified soils with 8% and 12% content was less than 5 mg/L, which met the requirements of the code, while the [Pb] of the cement solidified soils could not meet the limits of the code. Compared with BC mixtures with bentonite, cement cannot effectively immobilize high concentration of heavy metals in soil, which may be due to the retardation of hydration reaction of cement by [Pb] in soil.

Figure 3 (a) Age: 7 days (b) Age: 28 days
Fig. 3. TCLP test of lead dissolution in BC and PC solidified soils
3.3. Unconfined compressive strength

Fig. 4 shows the results of unconfined compressive strength of two kinds of solidified soils with different contents at 7 and 28 days of age. With the increase of age, the unconfined strength of the two kinds of solidified soils increases regardless of their content, and the increase of BC solidified soils is smaller than that of cement solidified soils. The main reason is due to the low cement content in BC mixtures. In addition, at the same age, the unconfined compressive strength of the two kinds of solidified soils increases with the increase of the amount of solidifying agent. The main reason is that the hydration reaction of cement occurs in the soil. The larger the amount of cement, the more hydrated calcium silicate (CSH) is produced, the stronger the strength is.

However, industrial pollution sites in China are mostly concentrated in the old urban areas and suburbs. With the continuous expansion of urban scale and the further transformation of urban layout, the remedied polluted sites need to be re-exploited and utilized urgently to alleviate the increasingly tense supply of urban land. Therefore, from the above aspects, the excessive strength of soil has brought difficulties to the secondary development and utilization of soil to a certain extent. The BC mixture of bentonite can not only satisfy the restoration effect, but also avoid the excessive strength of soil, which is convenient for land development and utilization.

![Fig 4. Unconfined compressive strength of solidified soil at 7-day and 28-day ages](image)

4. Summary and Conclusions

In this paper, the basic characteristics, dissolution characteristics and unconfined compressive strength of lead contaminated soil before and after solidification and remediation are studied. Based on the test results and analysis, the following conclusions are drawn:

1. Compared with PC-solidified soil, the pH and EC values of BC-solidified soil are lower, and the pH and EC values of 4% and 8% of BC-solidified soil meet the interval values needed for vegetation growth.

2. The dissolution of heavy metals in BC-solidified soil and PC-solidified soil decreases with the increase of the amount of solidifying agent, and the dissolution of heavy metals in BC-solidified soil is lower at the same amount of solidifying agent, which indicates that the mixed material (bentonite + cement) has better effect on the fixation of heavy metals.

3. The unconfined compressive test results show that the unconfined compressive strength of BC-stabilized soil and PC-stabilized soil increases with the increase of the content of solidifying agent, but compared with PC-stabilized soil, the unconfined compressive strength of BC-stabilized soil is smaller. Therefore, BC solidified soil can avoid excessive soil strength and facilitate the secondary development and utilization of contaminated land.
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