Properties of Solid Waste Mixture-Solidified Cu$^{2+}$-Contaminated Soil

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Abstract. To study the solidification effect of red mud, calcium carbide residue, and phosphogypsum mixture on Cu$^{2+}$-contaminated soil under the soaking condition, the stress-strain, leaching toxicity, and microstructure of solidified soil with cement and mixture were systematically analyzed. The results show that the peak stress of the mixture solidified soil increases with the curing age, and the addition of solid waste is beneficial for the improvement of peak stress. Its leaching concentration of copper ion is not only lower than that of cement solidified soil, but also lower than 0.6mg·L$^{-1}$. Besides, the leaching concentration decreased gradually with the curing age. According to the microstructure of solidified soil, it is found that the hydration products of the solidified soil are mainly represented by calcium silicate hydrate/calcium aluminosilicate hydrate and ettringite, which play an important role in the development of the strength and the solidification of copper ions.

Keywords: Cu$^{2+}$-contaminated soil, solid waste, leaching toxicity, microstructure.

1. Introduction

With the development of industrialization, heavy metal pollution is becoming more and more serious in China [1]. The pollution posed a serious threat to human health and the sustainable development of the ecosystem. Currently, various technologies have been developed to reduce the potential release of heavy metals into the environment. Among them, solidification/stabilization is a promising technology and used widely. After the treatment with a solidifier/stabilizer, the mechanical properties of the contaminated soil will be greatly improved [2].

Red mud is a kind of industrial solid waste produced in the process of alumina production [3]. Its dust and alkalinity will pollute the atmosphere, soil, and groundwater. Many scholars use it in the preparation of mine filling agents and cementitious materials [4], solidification of heavy metal contamination [5], remediation of contaminated soil [6], etc. Calcium carbide residue and phosphogypsum are industrial by-products. To recycle phosphogypsum and calcium carbide residue, scholars proposed to use them to prepare cementitious materials [7].

To reveal the interaction effect among the three kinds of solid wastes, the mechanical properties and microstructure of the mixture-solidified soil were tested and analyzed in this paper. At the same time, the mixture was used to solidify the Cu$^{2+}$-contaminated soil. Through the detection of the
leaching toxicity of Cu²⁺ ions, the influence of soaking conditions on the solidification effect was explored.

2. Materials and methods

2.1. Materials

The soil samples were obtained from a construction site in Taiyuan City, Shanxi province of P.R. China. It was bagged and transported to the laboratory for natural air drying. The dried soil was manually crushed and then mechanically sieved through a 2mm sieve mesh. Red mud, calcium carbide residue, and phosphogypsum are supplied by the factory. The cement is 42.5-grade ordinary Portland cement. The particle size distribution of materials is shown in Figure 1, and the chemical compositions are listed in Table 1.

Analytical grade Cu(NO₃)₂·3H₂O powder was used as heavy metal contained resource. The Cu²⁺ concentration is determined as the 10,000mg·kg⁻¹.

![Figure 1. The particle size distribution of materials.](image)

Table 1. Chemical composition of red mud, calcium carbide residue, and phosphogypsum

| Materials         | CaO  | Fe₂O₃ | Al₂O₃ | K₂O  | MgO  | Na₂O  | SO₃  | SiO₂ |
|-------------------|------|-------|-------|------|------|-------|------|------|
| Red mud           | 6.26 | 2.56  | 3.36  | 0.83 | 0.57 | 5.78  | 0.38 | 20.78|
| Phosphogypsum     | 21.77| 0.40  | 0.07  | 0.34 | 0.16 | 0.12  | 38.95| 19.27|
| Calcium carbide residue | 13.72| 0.08  | 0.05  | 0.03 | 0.02 | 0.77  | 0.89 | 10.80|

2.2. Methods

According to Zhang et al. [8] studies, the addition of a solidifier can increase the maximum dry density of soil and reduce its optimal moisture content. Based on the water content, determined by the Light Compaction Test results [9] and the additional content of the solidifier, the Cu²⁺ solution and soil were thoroughly mixed with a mechanical mixer for a few minutes to prepare the required concentration of Cu²⁺-contaminated soil. The prepared contaminated soil was sealed in an airtight bag and equilibria for 24 hours. After that, the contaminated soil was mixed and stirred with the solidifier to form the cylindrical test block by static pressing. In this paper, the solidified soil samples were numbered by SN0 (cement-solidified soil), GF0 (solid waste mixture-solidified soil), SN1 (cement-
solidified Cu\(^{2+}\)-contaminated soil), and GF1 (solid waste mixture-solidified Cu\(^{2+}\)-contaminated soil). The prepared samples were sealed and maintained in the standard curing box, and then soak in the water to the measured age.

The YHS-229WJ-50kN microcomputer-controlled electronic universal testing machine of Shanghai Yihuan Instrument Technology Co., Ltd was used to test the stress and strain values with a speed of 1mm·min\(^{-1}\). The test was carried out in the condition of no lateral restriction. On account of the solid waste and heavy metal that have been added to the soil, the leaching toxicity has to be tested in this study. The leaching toxicity of samples was tested as required by the Chinese standard [10]. Furthermore, the microscopic detection test was also carried out to analyze the microstructure of solidified soil.

3. Results and discussion

3.1. Stress-strain

The stress-strain curves of solidified soil at different curing ages are shown in Figure 2. The stress-strain curve of each solidified soil can be divided into three stages: (1) elastic-plastic deformation; (2) failure deformation; and (3) stable stage. The curves exhibit a gradual drop in the post-peak stress with strain. The peak stress of Cu\(^{2+}\)-contaminated soil solidified by red mud, calcium carbide residue, and phosphogypsum mixture increases with the soaking curing time, as well as the cement solidified soil. Comparing the figures, the peak stress of mixture solidified soil was bigger than that of cement solidified soil in the same condition. The addition of solid waste has an obvious positive effect on the peak stress of solidified soil. From the comparison of (c) and (d) or (a) and (b), it can be seen that the addition of Cu\(^{2+}\) ions have an obvious deterioration effect on the peak stress development of solidified soil. Comprehensive, the curing age enhanced the brittleness of solidified soil, while the Cu\(^{2+}\) ions strengthened the toughness of the solidified soil.

The red mud presents alkalinity, which can not only provide active substances for hydration reaction but also provide a favorable environment. The main component of solid waste carbide residue is Ca\((\text{OH})_2\), which promotes the formation of hydrate products in the specimen. As for the phosphogypsum, its main component is calcium sulfate, which forms calcium ion and sulfate ion after hydration and reacts with other active substances in the specimen to form ettringite (AFt). Within a certain amount of AFt, it can fill the internal structure and improve the integrity of the specimen. Besides, the alkaline environment provided by red mud and calcium carbide residue is not only conducive to the stable existence of AFt [11] but also makes colloidal ions dissolved in alkali gradually precipitate colloid, which plays a cementation role and increases the stress of the specimen [12]. Therefore, hydration reactions can undergo among red mud, carbide residue, and phosphogypsum, which can promote the peak stress of the specimen.
3.2. **Leaching toxicity**

The leaching toxicity is a powerful tool to determine the solidification efficiency of heavy metals in a solidification system. The leaching results of solid waste mixture-solidified soil and cement-solidified soil are shown in Figure 3. It can be seen that the leaching concentration of Cu$^{2+}$ ions gradually decrease with the curing age. Meanwhile, the leaching concentration at 28 days is significantly reduced compared with the previous period. Besides, the leaching concentrations of Cu$^{2+}$ ions are all less than 0.6mg·L$^{-1}$. Comparing the results of two kinds of solidified soil, it can be seen that the leaching concentration of Cu$^{2+}$ ions of solid waste mixture-solidified soil is less than that of cement solidified soil. It means that the addition of solid waste presents a better solidification effect of Cu$^{2+}$ ions than that of pure cement. What's more, all of the values satisfy the threshold of the Chinese standard [10]. All in all, compared with cement, the addition of solid waste may have a better effect on the solidification of Cu$^{2+}$ ions.

![Figure 2](image_url1)

**Figure 2.** The relationship between stress and strain.

![Figure 3](image_url2)

**Figure 3.** Leaching toxicity of solidified Cu$^{2+}$-contaminated soil.
3.3. Microscopic properties of solidified soil

As shown in Figure 4, the micromorphology of solidified soil with a magnification of 7000 times observed by the JSM-IT200 scanning electron microscope is shown. As can be seen, (a) is the cement-solidified Cu²⁺-contaminated soil, and (b) is solid waste mixture-solidified Cu²⁺-contaminated soil. For the cement-solidified Cu²⁺-contaminated soil, there are more holes between the particles than mixture-solidified soil. In solid waste mixture-solidified soil (b), there are two main forms of new products, while the main product is phase A in the cement solidified soil. The different substances lead to a denser structure. The flocculent substance (A) may be calcium silicate hydrate, and the obvious needle substance (B) may be ettringite. In alkaline conditions, Cu²⁺ ions can precipitate with OH⁻ ions. The hydration products have an adsorption effect on Cu²⁺ ions. Besides, Cu²⁺ ions have a replacement reaction with cations in ettringite, and they may be packed in ettringite [13].

![SEM of solidified Cu²⁺-contaminated soil](image)

**Figure 4.** The SEM of solidified Cu²⁺-contaminated soil (a) cement (b) mixture.

4. Conclusions

This study presented a systematic investigation on using the solid waste mixture to solidify the Cu²⁺-contaminated soil in the condition of soaking. Major conclusions can be drawn as follows:

1. The peak stress of Cu²⁺-contaminated soil solidified by mixture increases with the curing time. The addition of Cu²⁺ ions have a deterioration effect on the peak stress. Besides, compared with the cement-solidified soil, the addition of solid waste can significantly enhance the peak stress.

2. The curing age enhanced the brittleness, while the Cu²⁺ ions strengthened the toughness of the solidified soil. Besides, the leaching concentrations of Cu²⁺ ions are all less than 0.6mg·L⁻¹, and the leaching concentration of solid waste is less than that of cement-solidified soil.

3. Calcium silicate hydrate/calcium aluminosilicate hydrate and ettringite are the main products in the mixture-solidified soil, which play a key role in the solidification of Cu²⁺ ions.

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