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Study on Curing Mechanism of Magnesium Phosphate Cement to Contaminated Soil

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Heavy metal pollution poses a threat to environment and human health in modern times. In order to avoid it, the curing mechanism of magnesium phosphate cement to contaminated soil under acid rain is studied in this paper. The macro-micro test, leaching test and other tests are adopted to observe the changes of the test project from the micro-angle. With the continuous progress of hydration reaction of magnesium phosphate cement, the ability of acid and corrosion resistance of contaminated soil is greatly improved. Using magnesium phosphate cement can effectively modify the structure of contaminated soil, strengthen its resistance in each aspect, thus realizing the effect of resisting heavy metal pollution.

1. Introduction

China's modern industry is relatively developed, but such development has brought great damage to the environment and social groups. Heavy metal pollution is one of the major pollution that threatens the environment and the social groups at present. The main pollution metals include lead, mercury, chromium, cadmium and arsenic-like metals. Therefore, in order to combat such heavy metal pollution, China has launched the Twelfth Five-Year Plan for Comprehensive Prevention and Control of Heavy Metal Pollution. So far, how to carry out effective measures for the prevention and control of heavy metal pollution is the focus of attention at all levels of the society at present.

Under the acid rain, low-pH magnesium phosphate cement solidifies heavy metal contaminated soil. The mechanism behind it is very complicated. At present, there are few researches on this point both at home and abroad. Thus this paper studies it through many kinds of test methods such as micro-test and macro-mechanical test.

2. Literature review

Magnesium phosphate cement curing mechanism and hydration products are different from Portland cement, and the hydration reaction of magnesium phosphate cement is based on the exothermic reaction of acid-base neutralization and is a solution-diffusion mechanism. Magnesium phosphate cement is a new type of inorganic cementitious material with phosphate hydrate as the bonding phase, which is mainly produced by acid and alkali chemical reaction under acid condition by over - firing magnesium oxide and soluble phosphate. Compared with other inorganic binders, magnesium phosphate cements have high early strength, high density and good durability.

Compared to ordinary cement, phosphate cement has an additional advantage, that is, it can adjust the pH by adjusting the content of magnesium oxide and phosphate. Cherginets et al. used different proportions of magnesium oxide and phosphate to form acidic and alkaline cements to cure heavy metal contaminated soils (Cherginets et al., 2017); studies have shown that the pH value of phosphate solidified soil is 6-10, which is lower than that of Portland cement solidified soil. In recent years, Sandra Manso et al. studied the use of low-pH magnesium phosphate cement to expand the biological acceptance range. It uses the ratio of the different components of the cement itself to obtain a pH of 5.5-7.0 for the cement after 28 days of curing. However, the mechanism of curing contaminated soil with low-pH magnesium phosphate cement is not clear, and whether it can effectively resist the erosion of acid rain remains to be further studied.

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It has been reported at home and abroad that magnesium phosphate cement has been successfully used to solidify heavy metal contaminated soils. An important reason is that the solubility of heavy metal phosphates is very low. Wright reported the successful application of magnesium phosphate cement to solidify heavy metals in the United States. Argonne National Laboratories has been working on various wastes that have been solidified/stabilized with magnesium phosphate cement, and subsequently applied to solidified frozen soils and deep oil wells. Lindborg et al. summarized the research status of magnesium phosphate cement solidified radioactive waste, and studies showed that it has a good curing effect on radioactive materials (Lindborg et al., 2018). Zhou et al. studied the concentration of different phosphates and retarders in solidifying heavy metal contaminated soil and compared with the results of ordinary Portland cement curing. The soil was sandy soil and the heavy metals were Pb and Zn. The results showed that phosphate cement can significantly reduce the concentration of heavy metal filtrates, which was superior to Portland cement (Zhou et al., 2018). Kogbara used magnesium phosphate cement to cure/stabilize contaminated soils containing Cd, Cr, Pb, Ni, and Hg, indicating that magnesium phosphate cement was a simple and economical method of treating heavy metal contamination (Kogbara, 2017). There were also studies on the solidification/stabilization of lead with magnesium phosphate cement. The results showed that the leaching toxicity test result was one order of magnitude lower than the national standard. The Pb element was detected in the cement cured product by EDS. Lee et al. used MKPC to cure/stabilize nitrate solutions containing various heavy metals. The curing effect on Pb(II) and Cr(III) was still good under acidic and neutral conditions (Lee et al., 2018). Chen et al. used magnesium phosphate cement to cure contaminants containing Hg and HgCl2 and studied toxicity leaching with various methods (Chen et al., 2017). Chong et al. studied the mechanical properties of magnesium-potassium phosphate cements for stabilization/solidification (S/S) of heavy metal-rich galvanic wastes (Chong et al., 2018). Therefore, curing heavy metal contaminated soil with magnesium phosphate cement is an effective approach. However, the current research focuses on the characteristics of leaching, and the strength and permeability characteristics of the engineering characteristics of solidified heavy metals contaminated soil need further study.

Wu et al. simulated the characteristics of acid rain in Jiangsu Province and used potassium magnesium phosphate cement to cure/stabilize soils contaminated by heavy metals such as Pb, Cr, Cd, and Zn, and studied the effect of acid rain on leaching characteristics (Wu et al., 2017). A leaching test of simulated acid rain was performed in the study. The ratio of magnesium oxide and potassium dihydrogen phosphate was fixed in the test. There are no multiple choices of magnesium oxide and potassium dihydrogen phosphate ratios to select multiple pH MKPC cements, ie, the low pH characteristics of magnesium phosphate cements have not yet been considered; and engineering properties such as strength changes after acid rain have not been studied.

It can be concluded that due to the importance of the problem, domestic and foreign scholars have conducted preliminary studies on the problem of heavy metal-contaminated soil under acid rain conditions both on site and in the room. However, the types of heavy metals are not complete, such as the study of As; most of the existing researches are still limited to the analysis of leaching characteristics of solidified contaminated soils, and the conclusions obtained are not consistent; it has been recognized that insoluble high-strength complexes are formed under high pH conditions, and heavy metals will be dissolved again under low pH conditions. However, there are few researches on the mechanism and countermeasures of acid rain affecting heavy metal solidified soil, and there are even contradictory studies; the mechanism of curing low-pH magnesium phosphate cement for contaminated soil is not clear, and whether it can effectively resist the erosion of acid rain remains to be further studied. More importantly, there is a lack of reliable technical means to achieve prevention and control of heavy metal solidified soil acid rain erosion and maintain the structural integrity of solidified contaminated soil. Therefore, in order to effectively grasp the curing mechanism of phosphate cement on heavy metal contaminated soil under acid rain conditions, two major problems need to be solved: on the one hand, it is necessary to study the effect of acid rain on the solidification and stabilization of magnesium phosphate cement in combination with the characteristics of acid rain components in various regions; on the other hand, the effect of magnesium phosphate cement component under acid rain on the curing mechanism of heavy metal contaminated soil.

In summary, the mechanism of the effect of acid rain on heavy metal solidified soil in magnesium phosphate cement low-pH environment curing system has been studied deeply. It reveals the rules and influencing factors of the microstructure and macro-intensity variation of solidified heavy metal contaminated soil during the solidification process, and it establishes the correlation between macro-parameters such as the concentration and intensity of heavy metals; it reveals the mechanism of the effect of acid rain on the solidification of heavy metals in a magnesium phosphate cement curing system, and establishes the relationship between the intensity of heavy metal solidification characteristics, the concentration of leaching and the components that characterize acid rain, and the acidity parameters. Therefore, based on the above research status, this study aims at the erosion mechanism of acid rain on solidified heavy metal contaminated soil and the curing mechanism of cement on heavy metals. X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques are used to analyze the mineral phase transformation and microstructure morphology of the contaminated soil under acid rain erosion conditions. The initial pH of the simulated acid rain, the type of curing agent, and the influence of the addition of heavy metals on the microstructure of solidified soil are compared.

3. Methods

3.1 Main research contents

Acid rain infiltration will cause failure in solidification of heavy metal contaminated soil, heavy metal dissolution, and strength reduction. With combination of theoretical and experimental methods, this paper adopts phosphate cement with low-pH characteristics to carry out studies on curing mechanism of heavy metal contaminated soil under acid rain conditions. This article will mainly focus on the influence of acid rain on the curing of heavy metals by phosphate cement in order to reveal the curing mechanism of phosphate cement on heavy metal contaminated soils under acid rain conditions. The main contents are as follows.

Firstly, the study on leaching characteristics of heavy metals and the changing rules of cured body strength in magnesium phosphate cement curing system. The changes in the strength of solidified contaminated soil (unconfined compressive strength) is observed by UCStest. The leaching test is used to observe the changes in the leaching characteristics of the solidified contaminated soil. The semi-dynamic leaching (Tank) and long-term static circulation leaching are adopted to simulate acid rain and horizontal oscillation (Batch) is adopted for comparative study. The influencing factors include heavy metal type, concentration, acid rain effect, cement effect, curing age, etc. A variety of laboratory tests for up to 90 days are performed to compare the changing characteristics of leaching and strength. The microstructure of solidified heavy metal contaminated soils are observed microscopically by means of SEM (scanning electron microscopy). The transformation of mineral phases such as solidified products is observed by XRD (X-ray diffraction), to explore the relationship between the transformation of mineral phases and the strength of solidified soil.

Secondly, the corrosion mechanism of acid rain and the effect of acid rain on the solidification of heavy metals. According to typical acid rain components in East China, Central China and Southwest China, the acid rain with different acidity is prepared. The experiment with acid rain and that without are carried out for comparison. Combining with the pH changes during the curing process, the influencing mechanism of acid rain type and acidity on the macro-parameters such as composition, structure and strength of solidified soil, as well as the influencing mechanism on leaching characteristics are revealed on the basis of the above tests (the previous part).

3.2 Experimental materials

The soil used in the test is international standard sand (GB / T 17671-1999) certified by ISO9001, with particle size divided into three grades: coarse sand at 1.0-2.0 mm, middle sand at 0.5-1.0 mm, fine sand at 0.08 ~ 0.50mm, each accounting for 1/3. Thus the grade distribution is good. An appropriate quantity of standard sand are taken to carry out relevant geotechnical experiment and microscopic experiment. The basic physical property index and mineral composition of the sand obtained is as shown in Table 1. The particle size distribution of the standard sand is shown in Figure 1 below.

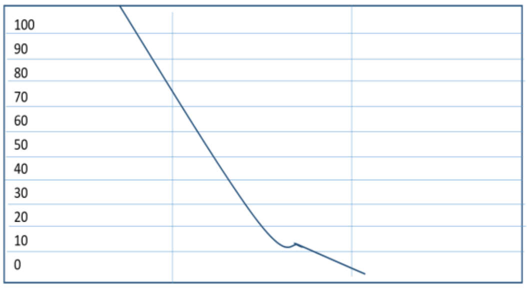

Figure 1: main mineral composition of standard sand

The test contaminated soil is made of artificially prepared mixed soil of standard sand + heavy metal, and the soil water content is determined according to the compaction curve. The self-made test soil sample is a simplified simulation of contaminated conditions for S / S study of contaminated soil. The purpose of using sand as raw material is that the absorbability of sand to heavy metals is poor, so that the adsorption of soil to metals can be reduced in the curing agent-soil-heavy metal-curing system, and the adsorption mechanism can be ignored, thus to reduce interference and improve pertinence for the curing mechanism analysis of contaminated soil in the later experiments. Mahasneh et al. found that in the sand + clay and sand + cement system, when the sand content is higher than 75%, the permeability of the system is significantly increased, and the leaching characteristics of contaminated soil are affected. In addition, when cement solidifies heavy metal contaminated soil as building repair material, adding appropriate amount of sand is helpful to improve the strength of cement-based materials.

Figure 2 is a compaction curve of plain soil obtained according to the compaction test specification (GB / T50123-1999). The optimum water content of the plain soil is 9.05%, the maximum dry density 1.86 g/cm3, the optimum water content of the M3 component 9.88%, the maximum dry density 1.99 g/cm3, the optimum water content of the M6 component 10.26%, and the maximum dry density 1.96 g/cm3. The optimum water content in CEMI group is 9.90%, and the maximum dry density 2.00 g/cm3. Therefore, in this experiment, the actual water content of cement-cured contaminated soil is 10%.

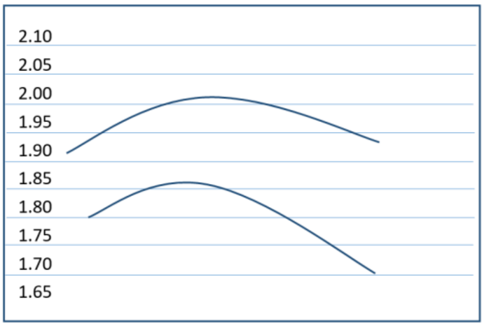

Figure 2: plain soil and solidified soil compaction curve (Moisture content (%))

3.3 Experimental content and methods

First, with the standard curing for 1, 3, 7, 28, and 90 days as a control, when the samples reached the specified age, they were subjected to unconfined compressive strength (UCS) test and batch leaching test after grinding. For the static circulation leaching test, the samples after 3-day pre-curing were placed in polyethylene tanks with simulated acid rain of pH = 2,4,7 respectively, which were subject to leaching for 1,3,7,28 and 90days respectively. After leaching reached to the specified age, UCS experiment, heavy metal leaching experiment and microstructure analysis were carried out. For the semi-dynamic leaching (Tank) experiment, the samples cured for 28days were put into a beaker filled with simulated acid rain with pH = 2,4,7 respectively. After 8 times of renewed leaching for 10days, the concentration of Zn2+ was measured successively, and the UCS and microscopic characteristics were measured after leaching. In the experiment, batch leaching was used to evaluate the chemical stability of heavy metal contaminated soil under acid rain, static circulation leaching experiment to predict the long-term leaching behavior and durability of heavy metal solidified contaminated soil, and semi-dynamic leaching experiment to estimate the release of Zn2 + from the leached components in different leaching periods, while maintaining the leaching trend of the components. Finally, the microstructure and curing mechanism of the solidified heavy metal contaminated soil after acid rain erosion were analyzed by scanning electron microscopy (SEM). Tables 3 and 4 show the specific test contents of MPC and CEMI cement solidified contaminated soil respectively.

Table 3MPC test contents of test samples for cement solidified contaminated soil

After that, the tests of unconfined compressive strength before and after leaching were carried out, and the leaching characteristics were studied.

In the tests of unconfined compressive strength before and after leaching, unconfined compressive strength (UCS) was used to measure the ability of the specimen to resist vertical stress. The test method for unconfined compressive strength of cement solidified contaminated soil sample is the same as that of the ordinary cement soil.

Figure 3: Unconfined compression apparatus

In the study of the leaching characteristics, long-term static circulation leaching, semi-dynamic (Tank) leaching and batch leaching were adopted. The effects of the kinds and concentrations of heavy metals on mechanical properties such as strength of solidified soil were studied, and the strength prediction models for heavy metal concentration, MKPC and curing age under the influence of specific acid rain were established. PH value of filtrate: the pH value of solution was measured by PHS-3C precision desk-type acidity meter produced by Shanghai Rex Analytical Instrument Factory; The initial pH value of artificial acid rain can be related to the pH value of the filtrate after leaching. The key factors affecting the solubility of heavy metals in solidified soil in acid rain were determined by measuring the pH and strength of solidified soil before and after leaching.

Figure 4: Static circulation leaching experiment

4. Results and discussions

Through the experimental study, the following conclusions can be drawn:
First, the results of Batch leaching, semi-dynamic leaching and long-term static leaching tests show that the concentration of Zn2 + in solidified contaminated soil with cement content of 15% is far lower than the limit specified by MEP (100mg / L), M3 and M6.
Second, the results of Batch leaching, semi-dynamic leaching and long-term static leaching tests show that there exist a leaching sequence between hydrolysis of MgO in MPC cement, and Ca (OH) 2 and Zn2 + formed by hydration reaction of ordinary cement. The dissolution of MgO and Ca (OH) 2 and other alkaline medium prior to the dissolution of metal ions causes changes in the pH value of the leaching solution, thereby further affecting the solubility of Zn2 + related compounds. In Batch leaching, the high alkalinity of CEMI cement has made the pH of the leaching solution too high, so that the leaching risk of Zn2+ is increased.

5. Conclusions

The present paper studies the appearance erosion, the characteristics of unconfined compressive strength and the variation law of stress and strain of cement-solidified zinc-contaminated soil under acid rain erosion, analyzes the effects of acid rain initial pH value, leaching time, curing agent type and heavy metal addition on the strength characteristics and uniaxial stress-strain characteristics of solidified heavy metal contaminated soil, and simulates the effects of acid rain on various engineering characteristics of curing contaminated soil by long-term static leaching and short-term semi-dynamic leaching.

Due to the diversity of contaminated soil and great differences in the soil quality in different regions, the standard sand is used to simulate the sandy soil in this paper, so as to exclude the disturbance caused by soil quality, which is far from the reality. Thus it is necessary to carry out further research on contaminated soil of different soil quality in different regions in the future. Since Zn2 + has a serious hindrance to the hydration reaction of ordinary portland cement, its pre-stage strength properties and leaching characteristics are not very satisfactory. Therefore, it is necessary to develop a modifier for ordinary cement to solidify zinc-contaminated soil.

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