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Effect of sulfate erosion on strength and leaching characteristic of stabilized heavy metal contaminated red clay

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Abstract: Solidification/stabilization (S/S) technology has been widely used for remediation of the heavy metal contaminated soils. The heavy metal ions will be leached from the stabilized contaminated soil under sulfate erosion conditions, which gives rise to secondary contamination to the areas around the mine sites. The commonly used Portland cement, fly ash and quicklime were taken as binder raw materials with various mix proportions. And then, the sulphuric acid and nitric acid method was used to investigate the leaching characteristic of stabilized heavy metal contaminated soils. The effects of binder types and binder contents, sulfate concentrations (1.5, 3.0 and 6.0 g/L) and erosion time (0, 7, 14 and 28 d) on leached concentrations of heavy metal ions from contaminated soils were studied. Moreover, a parameter named immobilization percentage (IP) was introduced to evaluate the influence of erosion time and sulfate concentration on immobilization effectiveness for heavy metal ions. The results showed that, the leached heavy metal concentrations increased with sulfate concentration and erosion time. Comparatively speaking, the composite binders that had calcium oxide in it exhibited the worst solidification effectiveness and the lowest immobilization percentage, with the largest leached heavy metal concentration.

Key words: solidification/stabilization; heavy metal contaminated soil; sulfate erosion; sulphuric acid and nitric acid method

1 Introduction

Exploitation of non-ferrous metal mines unavoidably causes environmental problem of heavy metal contamination to the soil and groundwater around the mine area. The heavy metal contaminations in such cases are mainly from mineral processing, effluent discharge, tailings and solid waste storage [1,2]. Previous study shows that lead (Pb) and zinc (Zn) contaminations in the mining area occupy a leading position [3,4], which is one of the most serious threats to the fitness of humans, animals and plants. For example, Pb affects the skeletal and intellectual development, and Zn leads to refractory anemia [5].

As for remediation of the heavy metal contaminated soils, solidification/stabilization (S/S) technology is widely used to solidify the heavy metal ions from migrating to surrounding areas and to strengthen the contaminated soils [6,7]. By contrast to other remediation technologies, S/S technology has the advantage of low cost, easy construction and excellent blocking capability to biodegradation [8].

The raw materials of S/S for heavy metal contaminated soil are usually high alkaline cement-hardening materials such as Portland cement, quicklime and fly ash [9], whose incorporation adjusts and changes the physicochemical properties of contaminated soil by physical absorption, chemical precipitation, coordination and oxidation-reduction. The chemical form of heavy metal ions in the contaminated soil can be changed from unstable state to stable state, and the migration and bioavailability of heavy metals are lowered to attain the remediation objective.

Sulphate attack is one of the common erosion phenomena, which could be caused by acid rain infiltration and industrial waste discharge etc and could lead to higher concentration of sulfate ion in groundwater. The acidic groundwater promotes the leaching of heavy metals like lead (Pb), zinc (Zn), cadmium (Cd) and manganese (Mn) from solidified/stabilized contaminated soil suffering sulphate attack [10]. Based on element

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samples, many researchers studied the leaching and hydraulic characteristics of solidified/stabilized heavy metal contaminated soil under the influence of acid rain, by using semi-dynamic leaching test [10−17], infiltration test and soaking test [18−21].

KAMON et al [18] deeply investigated the erosion mechanism of lime and cement stabilized soil subjected to acid rain through infiltration with soaking test and concluded that the engineering and physico-chemical properties of the stabilized soils would change during a long time of acid rain erosion. STANFORTH and QIU [22] studied the solubility of lead contaminated soil treated by phosphate-based additive, coming to the result that the addition of soluble phosphate greatly reduced lead solubility. MALVIYA and CHAUDHARY [11] investigated the immobilization effectiveness of various heavy metals (Pb, Zn, Cu, Fe and Mn) using diffusion leaching tests and geochemical modelling for cement solidified/stabilized hazardous sludge, concluding that the leaching process of heavy metals from solidified/stabilized soils was controlled by pH condition and metal hydroxide solubility. MOON et al [12−14] conducted a series of modified semi-dynamic leaching tests for quicklime/fly ash treated contaminated soil and evaluated the solidification/stabilization effectiveness with diffusion coefficient and leachability indices of the target heavy metals. DALMACIJA et al [23] investigated the long-term leaching behavior of Pb- and Cd-contaminated sediment by performing modified semi-dynamic leaching tests using acetic acid and humic acid solution as leachant, and the standard toxicity characteristic leaching procedure (TCLP) showed that S/S samples turned to be acceptable for "controlled utilization". SONG et al [15] performed semi-dynamic leaching test, toxicity characteristic leaching procedure (TCLP) and sequential extraction procedures, in which concentrated sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) solution was taken as leachant, and investigated the leaching characteristics of heavy metals in cement-based solidified/stabilized sewage sludge. More recently, DU et al [10,19] and JIANG et al [20] studied the effect of acid rain with various pH on leaching and hydraulic characteristics of cement-based solidified/ stabilized lead contaminated clay through infiltration and soaking tests, obtaining the results that the leached concentration and leaching rate of calcium were significantly influenced by pH of acid rain and the sulfate ions in it. The above-mentioned studies indicate that the controlling mechanism of leaching of most heavy metals from S/S treated contaminated soil is diffusion [12,14,23], while in some cases, the mechanism controlling heavy metals leached from stabilized soils is surface wash-off or wash-off and diffusion combination [11,13,24].

There have been abundant research achievements about leaching behaviors of heavy metal contaminated soils treated by solidification/stabilization, however, studies on mechanical and leaching characteristics of stabilized contaminated soils suffering secondary acid attack are still rare [18, 20−22].

The objective of this work is to investigate the influence of sulfate erosion on mechanical properties and leaching characteristics of cement based and composite cement/quicklime/fly ash based solidified/stabilized lead/zinc contaminated soil. A series of toxicity characteristic leaching procedures (TCLP) with sulphuric acid and nitric acid method were performed on Pb- and Zn-contaminated red clay that had been eroded to different extents. The influence of various possible factors including cement/quicklime/fly ash contents and proportions, concentration of sulfate solution, and erosion time of the solidified/stabilized soil in sulfate solution, on the leaching characteristics and mechanical properties of the soil was investigated, which can provide a basis for understanding the resistance capacity of binders for sulfate erosion.

2 Materials and method

2.1 Materials

The uncontaminated red clay used in this test was collected from the surrounding area of a nonferrous metal mine in Chenzhou City, China. The basic physical and chemical properties of the soils are summarized in Table 1. The water content was tested using gravimetric method as per HJ 613−2011 [25]. The Atterberg limits were tested as per GB/T 50123−1999 [26]. The pH of the soil was measured as per NY/T 1377−2007 [27]. The optimum water content and maximum dry density of the soil were determined as per the standard Proctor compaction test [26]. The chemical compositions of the uncontaminated red clay used in this work were determined by X-ray diffraction experiment, as listed in Table 2.

Table 1 Physico-chemical properties of soil used in this work

Property	Value
Natural water content, w_n/%	27.3
Specific gravity, G_s/(g·cm^{-3})	2.75
Plastic limit, w_P/%	22.6
Liquid limit, w_L/%	43.5
pH	7.93
Optimum water content, w_{op}/%	24.4
Maximum dry density, $\rho_{d,max}$/(g·cm^{-3})	1.79

The commonly used cement, fly ash and lime were chosen as the stabilizers. Cement used in the tests was ordinary #42.5 Portland cement produced in Tianjin, China, with a specific surface area of 370 m^2/kg. Fly ash