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Solidification/stabilization mechanism of Pb(II), Cd(II), Mn(II) and Cr(III) in fly ash based geopolymers

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HIGHLIGHTS

- Fly ash based geopolymers can effectively solidify heavy metal ions.
- The method has low cost and solidification effect is better.
- Different heavy metal ions have different influence on the geopolymers.
- The solidified mechanism was the physical fixation, adsorption and ion exchange.
- The pilot-scale test achieved the same results.

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ABSTRACT

Geopolymers are new cementitious materials, which can effectively solidify/stabilize heavy metal ions. Fly ash is an industrial waste from the coal-consumed power plant. With thermal power projects continuously building in the world and the emissions and accumulation quantities of fly ash are increasing yearly. At the same time, with the development of modern industry, waste and waste water containing heavy metals are continuously discharged, so that heavy metal pollution has been the very serious world environmental problems. Aiming at the problem of fly ash and heavy metal pollution, this study referred to solidification/stabilization (S/S) of Pb (II), Cd (II), Mn (II) and Cr (III) in fly ash based geopolymers prepared using composite activator of sodium silicate and sodium hydroxide. The solidification (S/S) results had been explained by means of the leaching and compressive strength of the solidification (S/S) geopolymers (solidified bodies) acquired. The analysis was performed through chemical analysis, X-ray Diffraction (XRD), Fourier Transform Infrared Spectrometer (FTIR), Scanning Electron Microscope (SEM), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and compressive strength tests. The results indicated that heavy metal ions could be effectively solidified in fly ash based geopolymers with a replacement of safe metal ions like Na (I) and Ca (II). Heavy metal ions had different effects on the compressive strength of geopolymers. (1.5 wt%) Pb (II) was beneficial to improve the compressive strength of geopolymers, and reached 49.34 MPa at 28 d. The XRD patterns indicated an amorphous structure and zeolite-like structure of aluminosilicate. The FTIR patterns study suggested changes of the Si-O-T (T = Si or Al) peak in the geopolymers. The SEM analysis revealed almost condensed homogenous surface of geopolymers. ICP-AES results showed that the geopolymer showed a high degree of solidification (S/S) of the heavy metal ions; in all samples, the solidification rates reached 99.9%. The mechanism of heavy metal ions being solidified was the interaction of physical fixation, adsorption and ion exchange. Finally, the pilot-scale test can achieve the same result on the basis of this study and made preparations for the future of industrialization.

1. Introduction

At present, with the development of industry, there is an increasing amount of heavy metal wastes generated from metalwork industry, chemical industry, electrical equipment manufacturing and other fields. It brings great damage to human beings and the environment. High concentrations of heavy metals in soil, water and air may cause bioaccumulation of heavy metals in animals and humans [1]. Heavy metals are classified as first pollutants in the world. Heavy metal pollution has become a very serious global environmental problem, and it is very serious [2].

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Most of the conventional methods are inefficient in heavy metal recovery, only transferring the contaminants from one phase to another one [3]. In recent years, solidification has become the central research focus due to its method simplicity, effectiveness, and low cost, and the solidified body which can be easily moved is a complete monolithic solid [4]. Geopolymers possess solidified properties that can effectively remove heavy metals [5,6]. Geopolymers solidification of heavy metals has many advantages [4]. Firstly, geopolymer has a three-dimensional network structure, and heavy metal pollutants can be "locked" in its structure. Secondly, the permeability coefficient of the geopolymer is very low, which can effectively prevent the rapid infiltration of heavy metal elements. Furthermore, in the process of geopolymer synthesis, Al (III) is a fourfold coordinated atoms, so [AlO4] has the ability to negatively charge and adsorb positive charge. In addition, the geopolymer is durable and resistant to weather, and simple processing.

Geopolymer is a hotspot in recent international research of new green cementitious materials. It is a kind of silicon oxygen tetrahedron and aluminum oxygen tetrahedron polymerized amorphous to semi crystalline aluminosilicate polymer [7]. It has a wide application prospect due to the excellent performance of organic polymer, ceramics and cement, and has the benefits of easily available raw materials, low prices, and simple preparation energy conservation and emission reduction [8]. Geopolymer can be used for coating adhesives, waste or toxic solid materials and new types of cement, and their raw materials can be some natural mineral or aluminosilicate waste [9]. Fly ash is the principal solid waste discharged from coal-fired power plants. In many countries, coal that produces a lot of fly ash is taken as the important foundation energy. The accumulation of large amount of the fly ash will cause serious environmental pollution every year [10]. Using fly ash to prepare geopolymer the solid waste can turn into treasure and at the same time it can reduce the pollution to environment [11]. The main reaction process of fly ash geopolymer: first of all, some aluminosilicate on the surface of fly ash has melted with the help of alkali-activator, and then migration, concentration and dispersed polymerization, and finally formed new amorphous gel phase of aluminosilicate [12]. The main source of fly ash geopolymer strength is the three-dimensional hydrated sodium aluminosilicate gel "N-A-S-H" produced during the process of geopolymer reaction [13].

Previous studies demonstrated that geopolymers that composed from metakaolin or wastes, such as fly ash, slag, and tailing could be solidified some heavy metals. Mallow et al. studies showed that heavy metal ions were involved in the reaction process of geopolymer [14]. In the study of Zhang et al. [15], they used the blast furnace slag and metakaolin as raw material to prepare geopolymer, and studied the solidify performance of geopolymer to Cu (II), and Pb (II), found that when slag 50%, geopolymer solid has the highest compressive strength, the solidification rate of Cu (II), and Pb (II) were above 98.5%. The Bankowski et al. [16] used the kaolinite geopolymers to solidify the harmful elements in the fly ash and found that when added fly ash 40%, the metakaolin geopolymers were able to solidify most of the harmful elements in the fly ash, the most significant solidifying effect among them were As, Cr and Cu, and the solidifying effect of heavy metal ions was reduced when the addition amount was too large. Between alkali solution and aluminosilicate powder weight ratio is usually between 0.2 and 0.5, but many studies reported that this weight ratio is above 0.35. Researchers tend to publish their research results in the form of patents and periodical articles, and still less realization with industrialization, which restricts the process of industrialization. At present, from bench test to commercial-scale application, solidification technology of geopolymer still has many problems to be investigated and solved. Many people do not understand characteristics of the geopolymer, and the geopolymer can replace cement in some areas are not accepted, which geopolymer applications have greatly hindered the promotion.

This study added heavy metal ions Pb (II), Cd (II), Mn (II), and Cr (III) respectively in fly ash geopolymers. The products and microstructures of the geopolymers material (solidified bodies) were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FIIR) and scanning electron microscopy (SEM). Finally, some pilot-tests were conducted on the basis of this study. The goals of this article were to research and evaluate the properties of solidified bodies and explain the mechanism of the solidification of heavy metal ions in fly ash geopolymers. This study provided the technical basis for industrialization of this kind of material. At the same time, this work can be used as evidence for the treating arsenic containing Pb (II), Cd (II), Mn (II) or Cr (III) waste materials. Preparation of geopolymers from heavy metals waste and fly ash can achieved the purpose of solidification of heavy metals, and the solidified bodies had certain value of use.

2. Experiment

2.1. Materials

Fly ash was obtained from a power plant in Ningxia (China). NaOH (AR), Cd $(NO_3)_2 \cdot 4H_2O$ (AR) and Cr $(NO_3)_3 \cdot 9H_2O$ (AR) were obtained from Tianjin Kermel Chemical Reagent Co. Ltd. $MnSO_4 \cdot H_2O$ (AR) was obtained from Beijing chemical plant. Sodium silicate solution was obtained from Panyu chemical plant, (8 wt% Na_2O, 25 wt% SiO_2 and 67 wt% H_2O, initial modulus (M = n (SiO_2)/n(Na_2O)) is 3.23). The composite activator was composed of NaOH and sodium silicate solution. NaOH was used to regulate sodium silicate solution to acquire composite activator whose modulus was 1.2.

The fly ash powder was dried in the oven (DHG-9070A) at 105 °C for 2 h, and the oven was closed into the sealed sample mill (HFZY-F4) when the oven was cooled to the room temperature. The powder obtained after grinding for 20 min was used as the experimental fly ash samples, and the particle size distribution was measured by the laser particle size distribution instrument (Microtrac-X-100). The test results were shown in Fig. 1 and d50 was 28.32 μm. X-ray Diffraction (XRD) test were conducted to assess mineralogy of fly ash, as showed in Fig. 2. The XRD patterns of fly ash (Fig. 2) showed a broad reflection (2θ) between 15 and 40 which an amorphous structure with a dominant phase of quartz, mullite.

The main component of fly ash was determined by chemical analysis, the main chemical component shown in Table 1. Accord-

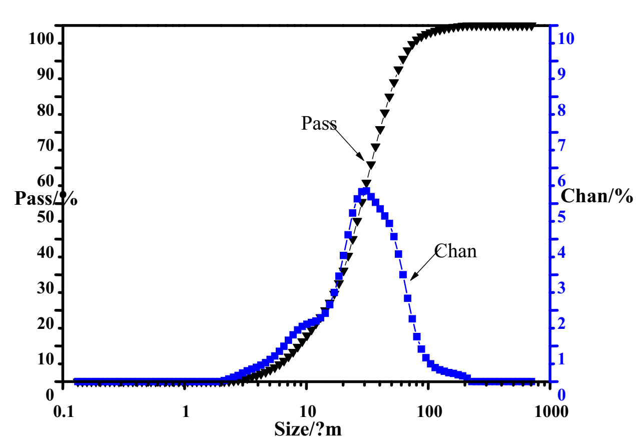

Fig. 1. Particle size distribution of fly ash.