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Original Research Paper

Heavy metal fixing and heat resistance abilities of coal fly ash-waste glass based geopolymers by hydrothermal hot pressing

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ABSTRACT

Hydrothermal hot pressing (HHP) was used to prepare high compressive strength fly ash-wasted glasses based geopolymers, which was subject to thermal analysis and the test of heat resistance as well as heavy metal solidification. Results showed that the geopolymers had good efficiency of encapsulating and fixing heavy metals. As for heavy metal element like Cu, Zn, Cd and Pb, the fixed efficiency reach at least 95%. Heat resistance test showed that the most mass-loss ratio of geopolymers was below 11.04% and the compressive strength was more than 55.27 MPa when it was calcined at 200–1000 °C for 2 h. During the calcining, geopolymers had gone through several main processes, including the evaporation of the free water, the bound water and constitutional water, the decomposition of carbonate, combustion of carbon, and crystallization reaction. XRD and FT-IR analysis showed that when calcined at 1000 °C, there produced several new crystallization phases with good heat resistance, including nepheline, kyanite, sillimanite. The improvement of this work does not only reflect that the hydrothermal hot pressing is featured by simple procedures, easy automation, timesaving and low cost, and also provide a long-term goal project, which could meet both demands: utilizing solid waste, saving resources and protecting the environment.

1. Introduction

Geopolymer is an amorphous inorganic polymer of three-dimensional network structure [1]. This salic inorganic material presents in the shape of aluminum-oxygen-silicate polymer composed of [AlO_4] and [SiO_4] tetrahedron with ionic bond and covalent bond as the main connection and van dee waals bond as the complementary connection [2]. If alkaline solution reacts with silicate mineral grain, gel phase will form on the surface of geopolymers. Gel phase after solidification and dehydration is called matrix phase which is either non-crystalline or semi-crystalline [3]. Though the matrix phase is in low strength itself, it connects the unreacted gel phase and forms into a material with good strength [4]. Geopolymers have high strength, resists to heat and burn and can solidify heavy metals [5,6]. Besides, geopolymers require low energy consumption and is of good durability. Owing to its gelation, it has extensive prospects used as high compressive strength material, solid waste material and glass material [7].

Coal fly ash is a suitable supplier of aluminum and silicon in the preparation for geopolymer. The main components of fly ash include non-crystalline solid, quartz, mullite ($3Al_2O_3{\cdot}2SiO_2$) and a small amount of unburned carbon [2,8]. Waste glass consists of above 80% silica (SiO_2) and some sodium oxide (Na_2O) or potassium oxide (K_2O) and calcium oxide (CaO) generally. The aluminum-silicon structure is depolymerized and polymerized into inorganic polymer, namely, the new type of inorganic gel material [9]. According to the feature of non-crystalline aluminosilicate and the reactions that occur at the glass-water interface, a special activator is used to activate fly ash and glass [10]. Coal fly ash with the addition of selected oxides was used for the preparation of a glass-ceramic with high mechanical properties [11].

At the present time, hydrothermal hot pressing (HHP) is widely applied to solidifying waste and synthesizing new functional materials [12,13]. In hydrothermal hot pressing, ion product is thousand times that of the value under normal temperature and pressure, which is the reason for its considerable increase in reaction rate. By hydrothermal hot pressing, the diagenetic process of cumulate that normally takes millions of years can be finished within a very short period of time [14]. At the temperature of 200 °C and under 8.5 MPa, a high-strength geopolymers (103.34 MPa) can be

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successfully prepared out of fly ash and wasted glasses (the mass ratio is 2:1) [15]. Such technique has a brilliant future owing to easy preparation and friendly environment.

In this paper, high-strength geopolymers with coal fly ash and wasted glasses are prepared by HHP method, and their heat resistance abilities, thermal analysis and solidification of heavy metals are investigated. And SEM, TG-DTA, XRD and FT-IR are used to further study the micro structure of geopolymers after heat resistance test.

2. Materials and method

2.1. Materials

Coal fly ash obtained from a power plant in Taiyuan, and its chemical components included 52.5% SiO_2, 31.2% Al_2O_3, 1.9% CaO and 5.9% Fe_2O_3 measured by XRF (S8 TIGER, Bruker, Germany). The loss on ignition in coal fly ash was 6.87%, which was measured according the GB/T 176-2008 (Methods for chemical analysis of cement). Glass powder were made from waste beer glass bottles by milling with the small-sized milling machine (SMΦ500 × 500 mm, Dongdong, China) for 3 h, and its chemical components included 66.0%SiO_2, 14.0% Na_2O, 8.0% CaO, 6.0% Al_2O_3 and others. The mean sizes of coal fly ash and glass powder were 22.92 μm and 15.45 μm, respectively, measured by the Particle Size Analyser (Eyetech/CIS, Ankersmid B.V., Holland). Sodium hydroxide, copper nitrate trihydrate, zinc nitrate hexahydrate, cadmium nitrate tetrahydrate, lead nitrate and acetic acid glacial used in this work were all analytic pure reagents.

2.2. Methods for preparation geopolymers

Fig. 1 was the schematic of geopolymers preparation and abilities test. The coal fly ash mixed with waste glasses by a mass ratio of 2:1 was used as starting materials, which were then mixed with 5 mol/L sodium hydroxide solution by a mass ratio of 4:1 (solid: liquid). The mixture was put into the Φ30mm reactor of hydrothermal hot pressing device (Tohoku University, Japan), whose structure was introduced in literature [15,16]. The mixture was subject to cold pressing for 5 min at room temperature and 8.5 MPa pressure, and then to hydrothermal hot pressing for 45 min at 200 °C and 8.5 MPa. After cooling down till the room temperature, the specimens were done for next abilities tests.

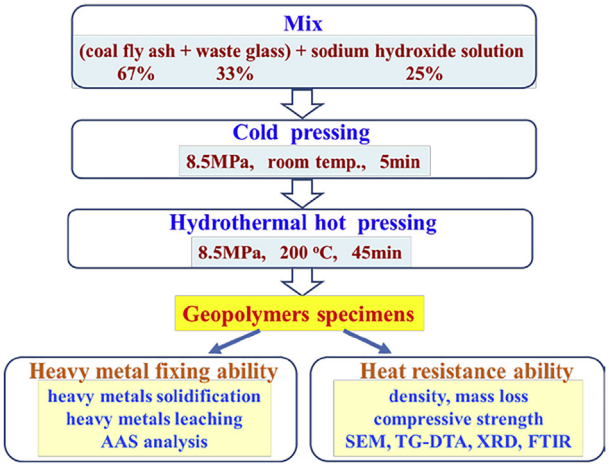

Fig. 1. Schematic of geopolymers preparation and abilities test.

2.3. Heavy metals solidification and leaching test

To order to study the fixing ability for heavy metals, HHP solidification for extra heavy metals was studied. Dissolved nitrate solution of heavy metals was added into the sodium hydroxide solution, which generated reaction solution with metal ion concentration of 0.5% (wt.). The solution was mixed with the solid materials by a mass ratio of 1:4 (liquid: solid), and then solidified in the HHP apparatus under optimal conditions listed in the Section 2.2. The contents of heavy metals in the resultant samples were: Sample A (Cu^{2+} 0.5%), Sample B (Zn^{2+} 0.5%), Sample C (Cd^{2+} 0.5%), Sample D (Pb^{2+} 0.5%), Sample E (Cu^{2+} 0.5%, Zn^{2+} 0.5%, Cd^{2+} 0.5%, Pb^{2+} 0.5%), Sample F (no heavy metal added).

The leaching tests were conducted based on the US EPA toxicity characteristic leaching procedure (TCLP) [17]. Specimens were pressed and ground into particles, and their diameter was less than 9.5 mm. Then, 2 g ground particles were put into glacial CH_3COOH by a ratio of 20:1 (liquid: solid). The mixtures were shaken in the homogeneous reactor (JBJX-8, Jianbang, China) at a speed of 30 rpm for 18 h. After settling for 30 min, the leachate was filtered by membrane filter of 0.45 μm [18]. The heavy metals leached from the Sample A ~ F were analyzed by the atomic absorption spectrometer (AAS, TAS-990, Puxi, China). In this paper, each experiment was repeated three times, and the average value was as the experimental result.

2.4. Heat resistance test

In order to prevent the specimens from exploring under high temperature, the specimens should be dried in the dying oven (CS101-2 EB, China) for 24 h under 80 °C [19]. The specimens were put in an electrically-heated muffle furnace. The temperature increased to 200 °C, 400 °C, 600 °C, 800 °C and 1000 °C at an incremental rate of 5 °C/min. The temperature was sustained at setting temperature for 2 h before the specimens were allowed to cool naturally to room temperature inside the furnace. And then, the mass loss and apparent density of the specimens were studied. The compressive strength of specimens was conducted by a pressure-measuring instrument (TYA-2000, China). The field emission scanning electron microscope (SEM, S-4800, Hitachi, Japan) was used to observe the micro structure, and the X-ray powder diffraction instrument (XRD, D2 Phaser, Bruker, Germany) was used to observe the phase variation of the specimens. The fourier transform infrared spectrometer (FTIR, Waltham, MA, USA), and the thermal analyzer (Setaram Setsys Evo, France) was used to conduct TG-DTA and thermal analysis at air atmosphere.

3. Results and discussion

3.1. Heavy metals fixing ability of geopolymers

Table 1 showed the effects of different heavy metals on the leaching data of specimens A ~ F. The fixed efficiency (Y) of metal ions in the solidified bodies was calculated by equation (1):

Table 1
Leaching concentration ($C_{leaching}$) of heavy metals from Samples A to F (mg/L).

Specimen	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
A (Cu^{2+} 0.5%)	**12.478**	0.213	0.041	0.565
B (Zn^{2+} 0.5%)	0.371	**1.477**	0.038	0.419
C (Cd^{2+} 0.5%)	0.252	0.219	**3.295**	0.341
D (Pb^{2+} 0.5%)	0.257	0.221	0.079	**2.831**
E (each 0.5%)	**20.406**	**3.258**	**3.829**	**3.153**
F (Blank)	0.360	0.232	0.030	0.403

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