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Comparison of red mud and coal gangue blended geopolymers synthesized through thermal activation and mechanical grinding preactivation

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HIGHLIGHTS

- Blended geopolymers based red mud and coal gangue synthesized through two methods.
- Mechanical grinding yielded better activity compared to calcination for the powder mixture.
- Two series geopolymer both yield excellent mechanical properties.

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ABSTRACT

Two binary geopolymers were prepared from the mixture of low-calcium bayer red mud and kaolinite-based coal gangue. The geopolymers were synthesized using two affordable and feasible methods mainly differed in preactivation and curing processes. The influence of the mix ratio of raw material and alkali activator on the compressive strength properties of two series geopolymers was investigated, and the optimal specimens of which were then determined. Furthermore, a comparative research on the mineral composition, crystal structure and microstructure of the superior geopolymers was performed through XRD, TG-DTA, and SEM-EDXS. Results revealed that GR8G2 was the optimum sample for the series geopolymer I and CR9G1 for geopolymer II. The compressive strength of all samples ranges from 15.05 to 30.25 MPa, the geopolymer synthesized from mechanical grinding preactivation displayed better developed strength. Mineral composition and microstructure studies indicated that both the final products are consist of amorphous silica-alumina-based geopolymer gels and some impurity fillers. This study showed that the two geopolymer synthesis methods for red mud and coal gangue were feasible, and the geopolymers may be applied as a new building material. Further studies are necessary to determine the optimal application parameters.

1. Introduction

Geopolymers are an innovative material produced through aluminosilicate natural materials or industrial byproducts [1–3]. Blended geopolymer is a polynary geopolymer synthesized through two or more aluminosilicate materials [4]. In recent years, blended geopolymer has attracted considerable attention. Various binary geopolymers, such as metakaolin/fly ash [5], metakaolin/red mud [6], fly ash/rice husk bark ash [7], red mud/fly ash [8], fly ash/slag [9], mine tailing and granulated slag [10], possess remarkable mechanical and chemical properties. The combination of these materials can cover the shortage of single raw materials in terms of chemical composition and chemical activity, and can benefit the alteration of Si/Al and Na/Al ratio in a geopolymer system [11]. Superior physical and chemical properties are still presented by this blended geopolymers, which has a wide application prospect in the field of building construction and transportation [12,13].

According to current reviews, kaolin or metakaolin (derived from calcined kaolin) was determined to be the original and popular source material of geopolymer [2,12,14,15]. Metakaolin based geopolymer was once the most established and stable products because of its pure and stable raw material composition. However, both natural kaolin and industrial synthetic kaolin are very

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expensive, and this drawback has restricted geopolymer development. Multitudinous solid waste resources therefore become a hot focus of the geopolymer sources. At present, both fly ash and red mud are popular source materials of blended geopolymers among numerous solid waste resources [15]. Incipiently, many researcher have devoted to studies of fly ash based blended geopolymers with other silicon aluminum sources as additives [16–19]. However, fly ash has become an important industrial raw materials rather than a solid waste because of its prominent pozzolanic activity. By considering raw material costs, red mud seems as an affordable choice for geopolymer synthesis. Red mud is a solid waste residue of the digestion of bauxite ores with caustic soda for alumina production [20]. He et al. synthesized red mud-fly ash-based and red mud-rice husk ash-based geopolymers successively, and have shown the effectiveness and feasibility of this blended geopolymer system from the resulting physical and chemical properties [8,21]. In the work of Ye et al. [22], alkali–thermal activation Bayer red mud based geopolymer is employed as solidification/stabilization reagent for municipal solid waste incineration fly ash, actually, which is a red mud and municipal solid waste incineration of fly ash based blended geopolymer. Generally, many researches devote themselves to the synthesis and characterization of red mud-metakaolin-based geopolymer [6,23,24], with the final aim of reducing metakaolin dosage.

Rather than reducing the consumption of kaolin, development metakaolin alternatives is preferred, thus, exploration of metakaolin alternatives is needed. Therefore, kaolinite-based coal gangue (also called coal-series kaolinite) [25], which is an unnoticeably abundant industrial waste with large reserves, seems to be a better choice. Preparation of metakaolin with coal gangue as raw material has been reported [26]. Coal gangue is a solid waste discharged during coal mining and washing, the pozzolanic reactivity of which can be improve under appropriate activated method [27]. The main mineral phases of kaolinite-based coal gangue is kaolinite. At present, research on geopolymer directly manufactured from coal gangue is extremely scarce. Composite cementitious materials based on red mud and coal gangue mixtures have been studied systematically [28–31]. However, all produces are calcium-silicon-aluminum-based binding materials, which are completely different system of cementitious material from geopolymer. By considering previous reports and facts about modified kaolinite, red mud has been successfully used in geopolymer synthesis. Therefore, geopolymer synthesis from both red mud and coal gangue is feasible.

According to a multitude of preparation methods of geopolymers and the finding of the previous exploratory working of the author [32], the current work presented two geopolymers derived from a mixture of red mud and coal gangue prepared from two different strategies. These approaches were mechanical activation-heat curing technology and thermal-alkali activation-room temperature curing technology. The present study aims to investigate the comparative mechanical properties, mineral composition and microstructure of the prepared geopolymers.

2. Materials and methods

2.1. Materials

Red mud, produced through Bayer process, was used for synthesis of geopolymers was obtained from Shandong branch Aluminum Corporation of China Limited, Zibo, China. The as-received red mud slurry with pH 12.7 and water content of 34.03%, was air-dried to below 3% moisture content and was broken to small pieces with hammer. This is a kind of low-calcium and high-iron red mud. The main chemical compositions are Al_2O_3, Fe_2O_3, SiO_2, and Na_2O. Coal gangue studied in this paper was dredged from Yangquan Coal Industry (Group), Yangquan, China, which is a kaolinite based gangue, that is, the main mineral composition is kaolinite. The coal gangue was subjected to grinding for 5 min through a planetary mill to allow sieving in 200 mesh [32]. The chemical composition and physical properties of the raw material is presented in Table 1, and the mineralogical phase is shown in Fig. 1. The alkaline liquid activator used was a mixture of sodium hydroxide (5M) and water glass (3.4M, 66 wt% H_2O). The prepared solution was stored at ambient temperature for at least 24 h.

2.2. Methods

The schematic diagrams of two inorganic polymers prepared from mechanical grinding and thermal activation are presented in Fig. 2. Preparation of geopolymer I consists of three steps: First, the mixture of red mud and coal gangue was milled for 20 min to Blaine's specific surface area of 22 m^2/g by a high-energy planetary ball mill. Then, the powdered mixture was mixed with the alkali-activator in a designed ratio and placed in a mold after stirring well. The precursor of alkali-activated pastes was treated by thermal curing at 80 °C for 24 h, and curing at room temperature for a predetermined age. This process was named as mechanical activation-heat curing technology. Geopolymer II was synthesized through thermal-alkali activation-room temperature curing technology. The red mud-coal gangue mixture was calcined at 800 °C for 2 h. After air-cooling to room temperature, the preactivation mixture was milled for 10 min, then mixed with alkali solution for preparation of geopolymer. Fresh pastes of inorganic polymers were cured at room temperature for 1, 7, 28 days to conduct evaluation tests. This process was named as thermal-alkali activation-room temperature curing technology.

Comparative investigations in this paper include mechanical properties and reaction mechanism. Mechanical property was characterized through compressive strength, which is reported as an average of three samples. Compressive strength of samples was measured using a WEW100 electronic universal tester (Wuxi, China). The reaction mechanism consisted of change in mineral composition, crystal structure, and microstructure, was characterized by X-ray diffraction (XRD, X'Pert Pro, PANalytical, Netherlands), Fourier transform infrared spectroscopy (FTIR, Continu μm IR Microscope, NICOLET 5700 FTIR Spectrometer, US), scanning electron microscope (SEM-EDS, Quanta 200, FEI, Holland)) and thermogravimetric analysis-differential thermal analysis (TG-DTA, Mettler Toledo, England).

3. Results and discussion

3.1. Mechanical properties

Generally, the mechanical properties of geopolymer derived from industrial byproducts are highly dependent on raw materials [4,33,34]. Two red mud-coal gangue blended geopolymers synthesized with different methods was presented. However, the raw material composition and the design of alkali activator were not fixed. Compressive strength analysis of the blended geopolymers was therefore employed for optimizing the raw material composition and selection of alkali-activator.

Fig. 3 shows the compressive strength development of geopolymer I (a) and geopolymer II (b) with the ratio of raw materials described in Table 2. The red mud to coal gangue ratios of geopolymer I and geopolymer II varied from 9:1 to 5:5, and the corresponding samples were named GR9G1, GR8G2, GR6G4, and GR5G5 for geopolymer I and CR9G1, CR8G2, CR6G4, and CR5G5 for geopolymer II. For all the alkali-activated geopolymers, the strength increased with curing age, but not all the samples showed outstanding compressive strength developments in this experimental condition. As shown in Fig. 3(a), GR8G2 reached a compressive strength of 10.25 MPa after curing for 1 day, with the ultimate strength halving until 7 days, and appeared superior among the series of geopolymer I. However, coal gangue promoted the initial setting of materials, as observed from the change in compressive strength after 1 day, and this trend disappeared with the progression of curing time. In particular, the content of the fixed raw material no longer controlled the strength at 28 days, but rather the ratio of SiO_2/Al_2O_3 and Na_2O/SiO_2 did, as many previously reported in similar materials [35]. The starting molar ratio of SiO_2/Al_2O_3 varies between 1.75 and 2.73 with the ratio of Na_2O/SiO_2 reduced from 1.05 to 0.73 (Table 2). If material strength was the only criterion in this study, then the optimum mole ratios for SiO_2:Al_2O_3 and Na_2O:SiO_2 of geopolymer I were 2 and 0.94, respectively, which corresponded to the results of other research [24,36]. Initial Si, Al, and Na contents greatly influence the geopolymerization process. Most researchers reported the variation range