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Thermal stability of a silica-rich vanadium tailing based geopolymer

Xiangke Jiao [a,b], Yimin Zhang [a,*], Tiejun Chen [a]

[a] College of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, China
[b] College of Resources and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

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ABSTRACT

With the rapid development of vanadium extraction from stone coal, large amounts of tailing were produced, which not only occupied vast land but also caused secondary environmental pollution. With the objective of comprehensive utilization of the secondary resources, the silica-rich vanadium tailing was converted into thermostable geopolymer. For geopolymer synthesis, the milled vanadium tailing was combined with fly ash and activated by sodium silicate. The geopolymer sample was heated at temperature of 150, 300, 450, 600, 750, 900 and 1050 °C, respectively. The milled vanadium tailing was obtained by dry ball milling of the raw vanadium tailing. Thermal stability of the geopolymer sample was evaluated in terms of the change of compressive strength and microstructure after heat treatment. Results showed that dry ball milling can effectively enhance the reactivity of the vanadium tailing. Compressive strength tests, SEM and FTIR analyses of the geopolymer sample before and after heat treatment indicated that its compressive strength increased at 900 °C, and apparent damage to its microstructure was not observed. These findings suggested that the vanadium tailing was potential for synthesizing fire-resistant geopolymer products.

1. Introduction

The geopolymer binders which are generally understood as alkaline activated aluminosilicates or an inorganic 2-component system consisting of reactive solid component and an alkaline activation solution [1], can act as eco-friendly alternative to ordinary Portland cements (OPCs). As a new kind of inorganic cementitious material, geopolymer is intrinsically fire resistant [2], due to its ceramic-like amorphous structure. Geopolymers are mostly synthesized from metakaolin [3], slag [4], fly ash [5] due to their high percentage of active Si and Al. But in fact many Si–Al materials could be used as a single source material or a combination for geopolymer synthesis [6,7]. Recently, amounts of tailing have increased with the rapid development of extractive industry. In China, much attention has been paid to research on vanadium extraction from stone coal due to the gross reserves of vanadium in stone coal accounts for more than 87% of the domestic reserve of vanadium [8], but extracting 1 ton of V_2O_5 generates 120–150 tons of tailing. Without proper practice, management of the vanadium tailing may incur cost and environmental pollution. A beneficial property of the vanadium tailing is that it contains reasonable amounts of Si and Al, which is the prerequisite of synthesizing geopolymer. However, the level of amorphous component of the vanadium tailing is very low and it consists mainly of quartz. Besides, previous research work showed that the amount of the reactive Al played an important role in the aluminosilicate gel formation [9]. The vanadium tailing shows extremely high Si/Al ratio, limiting the formation of a cross-linked geopolymer structure [10]. Thus it is unfavorable to use the vanadium tailing as source material for direct geopolymerization.

It is the objective of the present work to investigate the feasibility of geopolymer synthesis using the vanadium tailing as the main aluminosilicate source material. Dry ball milling was conducted on the raw vanadium tailing for enhancing its reactivity. Combined with fly ash as additional-Al source, the milled vanadium tailing was activated by sodium silicate to create geopolymer product. Thermal stability of the geopolymer sample was evaluated in terms of the change of compressive strength and microstructure after heat treatment.

2. Experimental work

2.1. Materials

A typical raw vanadium tailing was sourced from a mining company (Hubei, China). The raw vanadium tailing was pretreated by dry ball milling. Weight ratio of milling medium to powder and milling time were 10:1 and 60 min, respectively. Particle size distribution curves of the raw vanadium tailing and the milled vanadium tailing are shown in Fig. 1. The average size (d_{50}) of the raw vanadium tailing decreases from 31.08 μm for the raw vanadium tailing to 2.68 μm for the milled vanadium tailing, indicating that the ball milling process has destroyed a large proportion of the vanadium tailing particles.

* Corresponding author.
E-mail addresses: jxk8210@yahoo.com.cn, zym126135@126.com (Y. Zhang).

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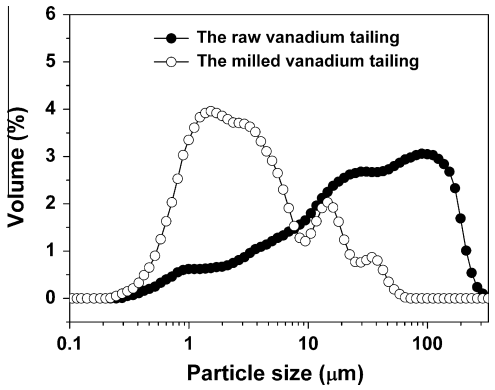

Fig. 1. Particle size distributions of the raw vanadium tailing and the milled vanadium tailing.

A fly ash was obtained from a local thermal power station in Wuhan. Chemical compositions of the raw vanadium tailing and the fly ash are shown in Table 1. It indicates that the main constituents of the raw vanadium tailing are Si and Al, which account for over 70% of the total weight. However, it contains too high Si and too low Al to produce geopolymer products. Recent research showed that addition of class F fly ash to copper mine tailing (which shows extremely high Si/Al ratio) can enhance the compressive strength of the copper mine tailing-based geopolymer [11]. The fly ash used in our experiment contains higher Al content than the raw vanadium tailing, so adding the fly ash in proper percentage could adjust the Si/Al ratio.

XRD patterns of the raw vanadium tailing and the fly ash are shown in Fig. 2. As indicated by Fig. 2a, crystalline quartz is the dominant phase in the raw vanadium tailing. As shown in Fig. 2b, the fly ash contains amorphous components (indicated by the hump) together with some phases such as quartz, mullite and hematite.

Considering that the alkaline solution frequently used by other researchers to dissolve the aluminosilicate source material was corrosive, and rapid dissolution of soluble Si was needed for accelerating geopolymeric reaction, a solid sodium silicate ($Na_2O{\cdot}1.5SiO_2$) purchased from a chemical company was used as activator. Distilled water was used to initiate geopolymeric reaction of the powdered precursors.

2.2. Sample preparation

To produce the geopolymer pastes, the Na/Al molar ratio and the H_2O/Na molar ratio were set at 1.0 and 1.6, respectively. Six mass ratios of the raw vanadium tailing to the fly ash (i.e., 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50) were used. The test results showed that, the mass ratio of 70/30 corresponded to the highest compressive strength. Thus the optimum Si/Al molar ratio was 3.3. Geopolymer sample of the composition (i.e., Si/Al = 3.3, Na/Al = 1.0 and H_2O/Na = 1.6), was selected and subjected to thermal stability test.

The procedure of synthesizing the selected geopolymer sample was as follows: The raw vanadium tailing, the fly ash and solid sodium silicate were mixed in a stainless steel container for 1 min; Then water was added to the powdered precursors and mixed for another 3 min; The fresh mixture was filled in a cylindrical mould of 50 mm diameter by 100 mm height and exposed to the pressure of 20 MPa for 30 s. Formed geopolymer sample was wrapped with plastic film and cured at room temperature (28 °C).

2.3. Tests and characterization

Leaching tests were conducted in an attempt to demonstrate the reactivity of the aluminosilicate source materials in geopolymeric reaction. Concentrated alkaline solution was applied for the leaching of the aluminosilicate source materials at high solution/solid ratios. One gram of the raw vanadium tailing (or the milled vanadium tailing) was mixed with 40 ml of NaOH solution (10 mol/L) at room temperature for 120 min using a magnetic stirrer. The solution was filtrated and neutralized by 37% HCl. Concentrations of Si and Al in the neutralized solution were determined using an Optima 4300DV inductively coupled plasma optical emission spectrometer (ICP-OES).

After 7-day curing periods, the geopolymer sample was removed from the plastic film, then placed in a muffle furnace and heated from room temperature to a target temperature of 150, 300, 450, 600, 750, 900 and 1050 °C, respectively. Heating rate was kept constant at 5 °C/min. Once the target temperature was attained, it was maintained for an additional 1 h. Then the furnace was switched off and the geopolymer sample was cooled naturally in the furnace to room temperature. Compressive strength and bulk density of the geopolymer sample before and after heat treatment were tested. Compressive strength was measured by a compression testing machine (YES-100) with a loading rate of 1 kN/S. Based on five replicated measurements, average value with standard deviation error was reported.

Thermogravimetric (TG) analysis was conducted on a NETZSCH STA 449c thermal analyzer (Germany). The geopolymer sample in powdered form was heated from 25 to 1100 °C in a nitrogen environment. Heating rate and nitrogen purging rate were 5 °C/min and 30 ml/min, respectively.

Particle size distributions of the raw vanadium tailing and the milled vanadium tailing were determined with a laser analyzer (Dandong, China).

Morphologies of the raw vanadium tailing and the milled vanadium tailing, as well as the geopolymer sample before and after heat treatment were analyzed using a JSM-5610LV scanning electron microscopy (SEM) (Japan).

The FTIR spectra for bulk bonding information of the raw vanadium tailing and the milled vanadium tailing, as well as the geopolymer sample before and after heat treatment were recorded using KBr discs on a Fourier-transform IR spectrometer (Nexus, Thermo Nicolet).

3. Results and discussion

3.1. Effect of dry ball milling on the vanadium tailing

Morphology of geopolymer products is mostly dependent on the morphology of source materials. Typical particle morphologies of the raw vanadium tailing and the milled vanadium tailing are shown in Fig. 3. After the milling process, the vanadium tailing appears different morphology. The raw vanadium tailing has coarse irregularly shaped particles with various dimensions. While the milled vanadium tailing presents more homogeneous and smaller particles, which is beneficial for the strength development of formed geopolymer products. This is consistent with the particle size analyses in Fig. 1.

FTIR spectra of the vanadium tailing before and after dry ball milling are shown in Fig. 4. The bands at approximately 1082 cm^{-1}, 797 cm^{-1} and 462 cm^{-1} are indicative of quartz. These bands have become broader in the milled vanadium tailing, which suggests that the milled vanadium tailing is more disordered than the raw vanadium tailing and the degree of crystallinity of quartz in the milled vanadium tailing decreases [12,13].

Results of leaching tests are presented in Table 2. It reveals that dissolution extents of both Si and Al from vanadium tailing can be significantly increased via dry ball milling, thus the reactivity of the vanadium tailing can be enhanced.

3.2. Thermal stability of the geopolymer sample

Residual mass, compressive strength and bulk density of the geopolymer sample at elevated temperatures are illustrated in Fig. 5. It shows that compressive strength does not change substantially before 600 °C. This phenomenon is linked to the fact that the geopolymer sample molded by compressing technique has relatively lower water content and more compact structure, leading to less shrinkage resulting from evaporation of water, which causes less thermal damage.

Before 600 °C, bulk density roughly matches with residual mass, suggesting that decrease of bulk density and residual mass are

Table 1
Chemical compositions of the raw vanadium tailing and the fly ash (wt.%).

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	V_2O_5	Loss on ignition
The raw vanadium tailing	64.17	10.27	4.98	4.46	2.06	5.27	0.14	1.15
The fly ash	52.12	28.44	3.82	4.11	2.05	0.50	–	5.89