Preparation of geopolymers from vanadium tailings by mechanical activation

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HIGHLIGHTS

- The paper provides a way to realize the efficiently utilization of vanadium tailings.
- The effect of mechanical activation on vanadium tailing is studied systematically.
- A method for reactivity evaluation of vanadium tailing was developed.

ARTICLE INFO

ABSTRACT

Because the vanadium tailings (VT) obtained from vanadium extraction are regarded as waste material with a low reuse rate, the recycling of VT is environmentally desirable and economically feasible. The main objective of this work was to investigate the feasibility of preparing geopolymers from low-reactivity and silica-rich VT by employing a new method, called mechanical activation (MA). The changes in the physicochemical properties and structure of the tailings before and after MA were explained by the determinations of particle size distribution, specific surface area, and the content of reactive components, as well as X-ray diffractometry (XRD) and Fourier transform infrared spectroscopy (FTIR). A calorimetric study was conducted to observe the geopolymerization process. The effect of MA on the resulting geopolymers was characterized by setting time, compressive strength, and resistance to chemical attack. The results show that MA is an effective method to improve the reactivity of the VT for geopolymer preparation. The maximum compressive strength of the activated-tailing based geopolymer (25 MPa) surpassed the strength (8.7 MPa) of the geopolymer based on the raw VT. In addition, activated geopolymers showed shorter setting times and better resistance to chemical attack.

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1. Introduction

Geopolymers are a new type of inorganic material consisting of tetrahedral SiO_4 and AlO_4 units, polycondensed into a three-dimensional structure under the reaction between aluminosilicate materials and alkaline activator [1]. Geopolymers exhibit good chemical and thermal stabilities, high compressive strength, and low permeability. In addition, the preparation of geopolymers is less costly and more energy-efficient than the production of Portland cement; the preparation process also emits 80% less CO_2, which makes it environmentally friendly. Thus, as a promising alternative cementitious product, it has attracted much attention

in recent years [2]. In general, many materials that are rich in silica and alumina can be used to prepare geopolymers, including meta-kaolin [3], fly ash [4,5], and even waste materials such as slag [6], tungsten tailings [7], and granite waste [8]. In China, large amounts of vanadium tailings (VT) have been accumulated because of the rapid development of vanadium extraction from stone coal; these tailings occupy vast tracts of land and pose a threat to the environment [9]. Thus, it is crucial to pay more attention to the utilization of VT as a potential material for geopolymer preparation, owing to the presence of silica and alumina oxides as the main components. However, VT has seldom received much attention for geopolymer preparation because of its low reactivity, which can result in poor performance of the geopolymers; in particular, the content of amorphous Si and Al, which are regarded as the main active ingredients reacting with the alkaline activator for the formation of geopolymer, is low and this limits its application. Thus, further

investigations are needed to improve the reactivity of VT and use it practically as a raw material for geopolymer preparation.

Recently, there have been many studies on the mechanical activation (MA) of solids for new materials or processes. The purpose of MA is to change the reactivity or physical-chemical properties of a solid. In particular, solid reactivity is induced by mechanical energy or a combination of mechanical and chemical effects through shearing, compression, extension, bending, and impact [10,11]. The improvement in solid reactivity is generally believed to be caused by repeated grinding leading to the dynamic creation of new fresh surfaces, defects in crystal structures, and phase transformations [12,13]. At present, the application of MA to improve solid activity has been applied in the field of cementitious materials. It was reported by Felekoğlu [14] that raw fly ash with coarse particles and low reactivity resulted in poor behavior of fly ash as a cementitious material; however, the physical and chemical properties of fly ash could be improved by MA, which enabled it to be used as a high-performance cement. Kumar et al. [15] showed that mechanically activated slag could achieve complete hydration without any chemical addition, and MA had a positive effect on the early strength development of the cement. Hounsi et al. [16] investigated the influence of MA of raw kaolin on the final compressive strength of geopolymers; MA was achieved by dry ball milling. The results showed that the compressive strength of geopolymers without MA was only 15 MPa after 28 d; however, after MA, the compressive strength of the obtained geopolymer reached more than 20 MPa, an improvement of 35%. Zhao et al. [17] showed that the particle distribution of circulating fluidized bed (CFB) fly ash was optimized by MA, which could also reduce the average pore size and volume. Meanwhile, MA reduced the polymerization of [SiO₄] and [AlO₆].

Various types of milling devices have been used for MA, and materials activated in different types of mills exhibited different effects [18,19]. The advantages of planetary milling are that the smaller size of the grinding media provides a larger contact surface between the media and the materials; moreover, the high agitator speed results in high kinetic energy of the media [20], which may open up the possibility of improving the reactivity of the tailings.

The main aim of this study was to investigate the feasibility of preparing geopolymers from low-reaction VT using MA. The effects of MA on the physical properties, including particle size, specific surface area, structure, and reactivity of the VT were investigated. The setting time, compressive strength, and resistance to chemical attack of mechanically activated-tailing based geopolymers were studied before and after MA. Furthermore, geopolymers were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to study the microstructure and phases that were formed.

2. Experimental

2.1. Materials

VT was supplied by a mining company in Hubei, China. Reactive Al was proved to be important to the formation of the three-dimensional structure of geopolymers in previous research [21]. The lower content of Al in VT was not conducive to aluminosilicate gel formation. Therefore, metakaolin (MK) was used as an

additional Al source. MK was obtained by calcining kaolin (Shandong, China) at 800 °C for 4 h. The chemical compositions of VT and MK determined by X-ray fluorescence (XRF) are listed in Table 1.

2.2. Methods

A laboratory planetary mill (QM-3SP4, Nanjing NanDa Instrument Plant) equipped with zirconia balls with different diameters (Φ30 mm, Φ40 mm, Φ50 mm, Φ70 mm) was used to activate the VT. The weight ratio of balls to tailings was 10:1, and the grinding concentration (C) was maintained constant at 50% during the milling experiments. The tailings milled for 1 h, 2.5 h, 4 h, and 5.5 h at 500 r/min will be referred as MAT-1, MAT-2, MAT-3, and MAT-4, respectively. The grinding concentration is defined by Eq. (1):

$$C = \frac{m_i}{m_i + m_r} \times 100\% \tag{1}$$

where C represents the grinding concentration; m_i is the tailing mass; and m_r is the water mass.

An alkaline dissolution leaching experiment was carried out to determine the content of reactive silica and aluminum in the tailings. The following preparation method was described by Jiao et al. [22]: 2 g of the raw tailings (or activated tailings) was added to a beaker containing 80 mL of NaOH solution (5 mol/L). The mixture was stirred using a magnetic stirrer at 50 °C for 2 h, after which 10 mL of HCl (37 wt%) was added to the beaker and stirred at ambient temperature for 30 min before filtration. Finally, the amount of silica and aluminum in the filtrate was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (PerkinElmer, America).

The alkaline activator was prepared by dissolving solid Na₂SiO₃·9H₂O in water at 70 °C, and then cooling the solution to room temperature. A geopolymer paste containing Si, Na, and Al in the molar ratios of 3:2:1, respectively, and a liquid/solid ratio of 0.36:1 (mass ratio) was prepared by mixing the raw tailings (or activated tailings) and MK with the alkaline activator solution. Then, the paste was cast into a 4 cm × 4 cm × 4 cm steel mold, sealed, and cured at room temperature for 7 d and 14 d, respectively. Geopolymer samples based on VT, MAT-1, MAT-2, MAT-3, and MAT-4 will be referred to as GVT, GM1, GM2, GM3, and GM4, respectively. After curing for 7 d, the resulting geopolymers were immersed in 5% sodium sulfate solutions or 3% sulfuric acid solutions for 28 days, their resistance to chemical attack was evaluated from the mass-loss rate in these solutions.

The particle size and specific surface area of the tailings were determined with a laser analyzer (Dandong, China) and a fully automatic specific surface area and porosity analyzer (BT-9300H, Bettersize, China). XRD was performed with an instrument from RIGIKU (D/MX-IIIa), using CuKα radiation with a Ni filter. The range of the scan angle was 10–70° with a step of 0.02° and a scanning speed of 10°/min. Fourier transform infrared spectra (FTIR) were acquired using a Thermo Nicolet (Nicolet6700) spectrometer. An isothermal conduction calorimeter (C80, SETARM, France) was used to study the geopolymerization rate. A calorimetric study was conducted at a constant temperature of 40 °C for 50 h. The raw tailings (or activated tailings) were mixed with MK in a 1:1

Table 1
Chemical composition of VT and MK (wt%).

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	TiO₂	SO₃	Na₂O	V₂O₅	Loss
VT	61.92	7.35	4.12	6.51	1.24	1.25	0.46	7.14	2.66	0.42	6.93
MK	53.27	44.58	0.70	0.02	0.13	0.53	0.29	0.22	0.34	–	–