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Fabrication and mechanism of cement-based waterproof material using silicate tailings from reverse flotation

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ABSTRACT

In this work, based on the surface hydrophobic characteristic of the reverse flotation tailings (RFT), the feasibility of fabricating cement-based waterproof material from RFT was investigated. The waterproof and mechanical properties of RFT mortars were evaluated by water absorption coefficient, contact angles and compressive strength. The results showed that RFT mortars presented lower water absorption coefficient of 21.1 $g/m^2\ s^{0.5}$ compared with 148.6 $g/m^2\ s^{0.5}$ for ordinary mortars. Moreover, both the internal and surface of the RFT mortars were hydrophobic, indicating the characteristic of the integral waterproof. Meanwhile, the compressive strength was hardly affected by the RFT as the raw materials. The waterproof mechanism of the cement mortars with RFT was performed by UV, SEM, XPS, FTIR and AFM. It was found that the origin of the hydrophobicity of RFT was the chemical adsorption between silicate particles and surfactant. Moreover, it was observed that RFT was in favor of early strength of the mortars through the investigation on hydration thermodynamical properties and kinetics behaviors of RFT.

1. Introduction

Mineral resources, widely used in the world, are important materials for social development. However, the massive tailings are produced due to the extensive exploitation of mineral resources. The annual emission load of tailings in the world is more than 14 billion tons [1], in which Chinese tailings discharge is over 1.5 billion tons. The tailings have caused a lot of environmental problems, such as land occupation, vegetation destruction, land degradation and desertification, dust pollution, surface and ground water pollution, etc. [2–5]. There are more than 9000 large and medium-sized mines in China, which cover an area of nearly 40 thousand km^2 and over 30% lands are taken by tailings [6]. Tailings are fine and easy to produce dust by long-term storage, which will cover vegetation and cause desertification etc. Moreover, Tailings containing heavy metal ions and chemical agents can result in water pollution. As time goes on, the heavy metal ions and chemical agents will transfer to other places and cause seriously negative impact on surrounding ecological environment [7–9]. Besides, when the tailings ponds used to store tailings are broken down, they will lead to great harm to the residents [10–14]. Tailings discharge also causes serious wasting of resources, because tailings contain a large number of valuable components. Therefore, how to dispose tailings reasonably has become a worldwide problem to be solved.

The utilization rate of tailings can reach more than 60% in some developed countries for investing lots of money and manpower to improve the treatment and utilization of tailings. However, at present, the utilization rate of mine tailings in China is very low (only 18.9%) [15,16]. In this sense, it is necessary to find a good treatment method based on tailings property, which can turn wastes into treasures and improve utilization rate.

Nowadays, the main recycling methods of tailings are as follows: 1) Tailings are re-processed again to obtain valuable components, which can improve the resource recovery rate and bring some economic benefits to the enterprise [17–23]. However, it cannot achieve large-scale utilization of tailings. 2) Dry discharge and reclamation of tailings are also a common treatment method [24,25]. It's beneficial to alleviate the potential safety hazard and the pressure of ecological restoration caused by tailings stacking. The defects using this method are increasing investments in the technology and equipment as well as more time in reclamation. 3) Tailings are used to fill mining area [26–28], which is one of the common treatments to dispose tailings in recent years to solve the problem of collapse in empty area. Nevertheless, tailings will pollute the underground water in the mining area. Hence the environmental impact assessment should be carried out before the tailings

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filled in the mining area. 4) Tailings are used to prepare materials [29–32]. Silva et al. [33] synthesized ceramic materials using iron tailings. As reported by Zhao et al. [34], eco-friendly autoclaved bricks were prepared by the utilization of hematite tailings. Kim et al. [35] prepared successfully low strength materials using arsenic-rich mine tailings. In the list of above, it could be found that the potential of tailings used in building materials is huge due to its superior properties (low cost, low pollution and high usage).

At present, the most widely used method of mineral processing is flotation, which includes direct and reverse flotation. For the direct flotation, the objective mineral was collected and brought out of the flotation cell. However, for the reverse flotation, there were quantity surfactants adsorbed on the surface of gangue minerals, which were brought out by air bubbles to form the reverse flotation tailings (RFT). The hydrophilic groups of the surfactants have the characteristic adsorption with RFT and the hydrophobic groups arrange outward to form a hydrophobic layer on the surface of RFT, leading to the hydrophobic property of RFT [36]. On the other hand, the objective minerals in flotation are usually metal elements, such as copper, lead, zinc, etc., while tailings are generally silicate minerals, which show the similar chemical composition with the aggregate in the mortars. Because of the characteristics of hydrophobic surface and silicate composition, RFT have the great potential value in waterproof building materials. Unfortunately, RFT were generally discharged in the dam or only used as the aggregates in the building materials like the common tailings mentioned above, and the hydrophobic characteristics of the RFT were not applied effectively [37,38]. Recently, waterproof mortars are commonly fabricated by adding a large amount of synthetic organic polymers to achieve the waterproof effect, which increase the cost significantly.

In this work, the feasibility of a novel approach to utilization of RFT, fabricating cement-based waterproof mortars with RFT, was investigated. The RFT was used to replace the waterproof agent and aggregates in the mortars to reduce the cost. The waterproof and mechanical properties were measured compared with the ordinary mortars. Moreover, the waterproof mechanisms of the RFT mortars and thermodynamical properties and kinetics behavior of RFT were also explained.

2. Experimental

2.1. Materials

The silicate mineral was obtained from Lingshou dressing plant in Hebei province. The XRD spectrum (Fig. 1) showed that the main mineral phase in silicate mineral was quartz. In addition, a spot of mica also

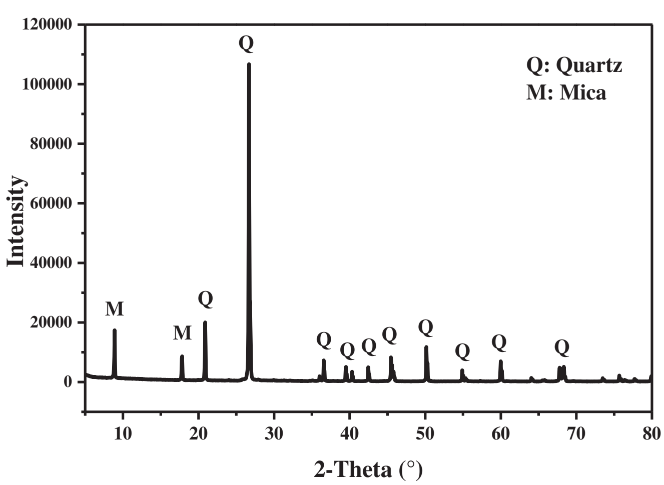

Fig. 1. XRD pattern of the silicate minerals.

existed. The main composition of the silicate mineral were silicon dioxide and aluminum oxide and the loss of ignition (LOI) was only 0.735% (Table 1), which satisfied the requirement of the raw material of the cement mortar. The particle size distribution of the silicate mineral was presented in Fig. 2. The particle size of the silicate mineral was concentrated between 10 μm and 100 μm and its specific gravity is 2.648 g/cm^3. The cement (grade 42.5, Chinese National Standards) was purchased from Huaxin Cement Co. Ltd.

Sodium oleate (NaOL, CP) was used as collector for silicate mineral. Calcium chloride ($CaCl_2$, AR) as activator and sodium hydroxide (NaOH, AR) as pH regulator in the reverse flotation were purchased from the Sinopharm Chemical Reagent Co. Ltd., China. The water used in this work was deionized water from Milli-Q Direct 16.

2.2. Preparation method

2.2.1. Preparation of RFT

To fabricate the RFT in the laboratory, the process and parameters were chosen according to the general dressing plants. Firstly, the surface of silicate mineral was activated by $CaCl_2$ solution under the alkaline condition (pH 12) adjusted using NaOH solution (1 M). Then, the silicate mineral was collected by NaOL as the RFT in the experiment. The dosage of $CaCl_2$ in silicate mineral was 550 g/t and the dosage of NaOL in silicate mineral was 3000 g/t.

2.2.2. Fabrication of cement mortars

To fabricate the cement mortars, the ratio of cement and silicate mineral (or RFT) was 1:3 by mass. The ordinary mortars from silicate mineral without reverse flotation were as control group. The water with proportion of 38% was added in the mixture of cement and silicate mineral. Then water, cement and silicate mineral were blended for 2 min at low speed and 1 min at high speed. After agitation, the mortars were molded in 50 × 50 × 50 mm steel mold. Then a MODEL ZS-15 jolting table was used to compact mortars and to remove air bubbles and voids [39]. The mortars were stored at the room temperature for 24 h before demolding. After demolding, samples were cured in the Numerical Control Standard Cement Conservation Box (20 ± 1 °C, 95% relative humidity) for 3, 7 and 28 days. The waterproof and mechanical properties of the specimens were tested after curing time.

2.3. Measurements

The particle size distribution of the silicate mineral was measured by Laser Particle Analyzer (APA2000, Malvern).

The main mineral phase composition of silicate mineral was determined using X-Ray Diffraction (XRD) at 50 mA, 40 kV Cu target.

The chemical composition of silicate mineral was determined through X-Ray Fluorescence Spectrometer (XRF, AXIOS, PANalytical.B.V).

The waterproof property was tested according to standard BS-EN 1925–1999 [40] after curing for 3 d, 7 d and 28 d. Specific operation was as follow: the dried specimens were weighed and placed in the tank, whose bases were immersed in the water to a depth of (3 ± 1) mm. The water level maintained constant by adding water as necessary. At time intervals, the immersed part was lightly dried using a damp cloth to remove all water droplets and weighed immediately, which was repeated until the weight was constant.

The contact angles of cement mortars were measured using KRUSS Tension Meters (K100, Germany). The cement mortars were pressed

Table 1
Chemical composition of the silicate mineral (wt%).

Composition	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO
Silicate mineral	0.101	0.020	3.799	93.77	0.056	0.037	0.0837	0.082
Composition	TiO_2	Fe_2O_3	Rb_2O	SrO	ZrO_2	Cl	LOI	
Silicate mineral	0.123	0.397	0.003	0.002	0.014	0.025	0.735	