Temperature effect on preparation of water-Storage ceramic foam with vanadium-titanium magnetite tailings

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Abstract. Massive accumulation of vanadium-titanium magnetite tailings (VTMT)—a kind of common industrial solid wastes—will pose enormous harms to both ecological environment and economic development. Based on the preparation of water-storage ceramic foam by taking full advantages of 50 wt% VTMT and 50 wt% waste glass, the effect of sintering temperature on the sample performance was further investigated through a test, and the foaming mechanism at high temperature was deeply probed. The results show that as the sintering temperature rises, the bulk density and compressive strength of the sample gradually decline, its water absorption per volume reaches the maximum value and the average pore diameter inside the sample is gradually increasing. The optimal sinter temperature is 1,040 °C, and the water absorption, bulk density and compressive strength of the sample are 56.5%, 0.26 g/cm³ and 0.68 MPa, respectively.

1. Introduction.
Cleaner production and comprehensive utilization of resources are eternal themes of industrial development, and the “zero waste” concept has aroused high attention both home (China) and abroad [1]. The gross reserves of vanadium-titanium magnetite tailings (VTMT), which are mainly distributed in Panzhihua City of Sichuan Province and Chengde City of Hebei Province in China, take the third place in the world. Though considerable economic benefits being acquired, tailings are heaped in quantity in local tailings ponds. There are about 570 million tons of VTMT in Panzhihua region, but the comprehensive utilization rate of the tailings is only 11.3% or so [2]. These accumulated tailings will lead to local land degeneration and groundwater pollution and increase the incidence rate of respiratory diseases among local residents [3]. Hence, an effective recovery technique is urgently needed to solve the industrial solid wastes pile-up problem.

The present main VTMT recycling methods in China and abroad include comprehensive V-Ti-Fe recovery, pit backfilling and preparation of ceramic foam materials [4,5]. Relatively speaking, preparing ceramic foam entirely by using the tailings can not only avoid secondary industrial solid wastes but also further improve the comprehensive utilization rate of the tailings. Water-storage ceramic foam is a new-type garden building material, and the internal pores it contains can store rainwater very well, improve the water-holding capacity of soil and reduce the water consumption of urban landscapes. This material can not only satisfy the national sponge city construction concept but also can effectively relieve the urban heat island phenomenon [6].
This study aims to realize the value-added VTMT utilization with low energy consumption. Following the preparation of water-storage ceramic foam with VTMT and waste glass, the effect of sintering temperature on material performance was further studied through a test. In addition, the high-temperature foaming mechanism of ceramic foam was experimentally explored.

2. Experiment

2.1 Raw materials
VTMT from Panzhihua Iron & Steel Group Co., Ltd, waste glass (Shenyang) and quartz were used as the main raw materials. Both foaming agent silicon carbide (SiC) and foam stabilizer sodium phosphate (Na₃PO₄) were purchased from Sinopharm Chemical Reagent Co., Ltd. In order to guarantee uniform particle size of the raw ceramic materials, VTMT were grinded and sieved through a 180-mesh sieve, and the tailings particles smaller than 77.2 μm accounted for 90%.

The main chemical compositions of the raw materials are listed in Table 1. From Table 1, the main chemical compositions in VTMT are SiO₂, alkali metal and alkaline earth metal oxide. As a flux-type raw material, waste glass has high K₂O and Na₂O contents, and can effectively lower the material sintering temperature.

| Raw material | SiO₂ | Al₂O₃ | CaO | MgO | K₂O | Na₂O | FeO | Fe₂O₃ | TiO₂ | Others |
|--------------|------|-------|-----|-----|-----|------|-----|-------|------|--------|
| VTMT         | 37.59| 9.27  | 11.48| 7.83| 0.97| 1.75 | 7.74| 7.70  | 9.70 | 5.97   |
| Glass        | 60.74| 17.86 | 1.93 | 0.92| 9.08| 4.98 | -   | -     | -    | 4.49   |
| Quartz       | 99.01| -     | -   | -   | -   | -    | -   | -     | -    | 0.99   |

2.2 Sample preparation and performance detection
50.0 wt% VTMT and 50.0 wt% waste glass were used as the main raw materials, along with 3.0 wt% quartz, 0.3 wt% SiC and 3.0 wt% Na₃PO₄ as additives. The raw materials and additives were mixed in a mixer for 60 min. Manual granulation (particle diameter:178-425 μm) was conducted after the ceramic slurry was dried. In the end, the ceramic particles were weighed and placed in a corundum crucible paved with aluminum silicate flame-proof paper, and then they were oscillated, spread out and gently pressed. The corundum crucible was put into a high-temperature box-type furnace, the sinter temperature was set as 1,000-1,080℃, and the temperature was held for 15 min. The samples were marked as A1, A2, A3, A4 and A5, respectively.

The bulk density of each sample was mass to volume ratio after sample cutting. The sizes of 80 pores in the sample were determined, and the average pore size was namely the average pore diameter. The compressive strength was determined via a universal electronic testing machine. The sample was boiled in water for 2 h and then taken out. The calculation formula for water absorption of ceramic foam is shown in Equation (1). The water absorption \(W_T\) is the change percentage after the sample mass \(m_1\) after water absorption is deducted by its mass \(m_0\) before water absorption, the sample volume is \(V_1\), and 1 g/cm³ is water density.

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W_T = \frac{(m_1 - m_0)}{(V_1 \times 1g/cm^3)} \times 100
\]  

3. Results and discussion

3.1 Determination results of bulk density and water absorption of the samples
The temperature effects on bulk density and water absorption of the samples are presented in Figure 1. As the sintering temperature increased, the sample bulk density gradually declined; At sintering temperature of 1,040 °C, the water absorption reached a maximum value. The sample bulk density and water absorption were 0.85 g/cm³ and 40.5%, respectively, at 1,000 °C, mainly because no sufficient liquid phases could be generated inside the sample and bubble growth was impeded. On the other hand, the reaction rate of foaming agent was slowed down under low-temperature state, which led to
insufficient gas yield. When the sintering temperature was 1,040 °C, the sample bulk density and water absorption were 0.26 g/cm³ and 56.5%, respectively, and the material performance became optimal at the time. Moreover, the gas-liquid balance was reached inside the sample and bubbles grew adequately and stably. As the temperature continued to rise, a large number of liquid phases were generated inside the sample and the bubbles were mutually fused, and thus the sample performance turned poor.

Figure 1. Temperature effects on bulk density and water absorption of samples.

3.2. Test results of compressive strength and average pore diameter of the samples
The temperature effects on compressive strength and pore diameter of the samples are expressed in Figure 2. It could be seen from the figure that as the temperature increased, the compressive strength of each sample was gradually reduced while the average pore diameter increased. The compressive strength reached the maximum value 0.91 MPa at sintering temperature of 1,000 °C. At low temperature, a few liquid phases were produced inside the melt, minute bubbles failed to fully grow up in the melt, so the inside sample became compact, and the maximum compression was borne on the material matrix of unit area. The compressive strength and average pore size of sample A3 were 0.68 MPa and 0.32 cm, respectively, at 1,040 °C. When the temperature increased, the compressive strength of sample A5 declined to 0.47 MPa and the average pore diameter was 0.63 cm, which was mainly ascribed to the existence of a large quantity of cavities and intercommunicating pores. These cavities and intercommunicating pores destructed the 3D porous structure inside the sample and resulted in poor material performance.

Figure 2. Temperature effects on compressive strength and average pore size of samples.

3.3. Morphological analysis of the samples
Figure 3 shows micrographs of the samples at different sintering temperatures. The difference sintering temperatures exerted major effects on pore size, distribution pattern and shape of the samples. The internal pore size of each sample was gradually enlarged as the temperature rose. From Figure 3, the pore size was nonuniform and no independent pores were formed in sample A2, and the material
bulk density and compressive strength were large at the time. The pore diameter of sample A3 ranged from 0.3 to 0.4 cm, the pore distribution presented approximately circular shape, there were few defective pores inside the material, and the sample was of favorable material performance at the time. Large fusion holes started appearing on the surface of sample A4 with nonuniform pore distribution. To figure out why, with an increasing quantity of liquid phases inside the sample, minute bubbles were continuously fused in the ascending process and larger bubbles were then formed. Through a comprehensive analysis, both pore distribution inside the samples and material performance became relatively optimal at sintering temperature of 1,040 °C.

3.4. Phase analysis
The XRD patterns of the samples at different sintering temperatures are shown in Figure 4. The main phases of the samples included wollastonite (CaSiO$_3$), diopside (CaMgSi$_2$O$_6$), feldspar, pseudobrookite (Fe$_2$TiO$_5$) and hematite (Fe$_2$O$_3$). The peak value of feldspar phase declined as the temperature increased, but the reduction amplitude was not evident, indicating that the feldspar phase in the high-temperature melt just started fusing and a small quantity of feldspar-phase minerals underwent decomposition.

3.5. Foaming mechanism
The SiC surface contacting the air was oxidized first during the heating process, so as to form a compact amorphous SiO$_2$ protective film. The SiO$_2$ protective film effectively obstructed oxygen penetration rate and made the whole reaction slow. As the temperature further increased, the SiO$_2$ protective film formed on SiC surface could easily react with alkaline melt or alkaline salt to form
liquid silicate phase, and consequently, the protective layer was corroded or destructed, the channels for oxygen to penetrate inside were increased, the oxygen diffusion was then accelerated, and thus a large quantity of CO or CO₂ gases were generated [7]. The proper sintering temperature contributed to uniform bubble growth inside the melt, and a ceramic foam material with excellent performance was formed with surface cooling. When the temperature was excessively high, the internal and external pressure difference of the bubbles turned large, the minute bubbles were inclined to rupture and fusion during the ascending process, and as a result, many defective holes were formed inside the sample [8].

4. Conclusions
The following conclusions can be drawn based on the above research contents:

(1) As the sintering temperature rises, the bulk density and compressive strength of the samples are gradually reduced, the water absorption per volume reaches the maximum value, and the average pore diameter inside the samples is gradually increased.

(2) After the water-storage ceramic foam material is prepared by taking VTMT and waste glass as the main raw materials, the water absorption (optimal), bulk density and compressive strength of the material are 56.5%, 0.26 g/cm³ and 0.68 MPa, respectively, at sintering temperature of 1,040 ℃ and holding time of 15 min.

(3) This study provides a feasible scheme for resource utilization of VTMT and conforms to the national sponge city construction concept.

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