Research Article

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Influence of polyvinyl alcohol–glutaraldehyde on properties of thermal insulation pipe from blast furnace slag fiber

https://doi.org/10.1515/htmp-2020-0085
received February 04, 2020; accepted July 29, 2020

Abstract: The development of an environmentally friendly binder can immensely benefit and promote the BF slag fiber industry. Accordingly, in this study, fiber insulation pipes were prepared using water glass, polyvinyl alcohol (PVA), and PVA–glutaraldehyde (GA); moreover, their bulk density, moisture absorption capacity, and thermal conductivity coefficient were measured and compared. The results demonstrated that the values of these three parameters depend on the binder concentration and dosage under certain fiber quality, pipe sizes, and manufacturing process conditions. The best binder composition was proven to be that of PVA–GA, prepared using 3 wt% PVA and 5 wt% GA herein, which facilitated reduction in the bulk density and improvement of the waterproof properties and insulation performance of the slag fiber pipes.

Keywords: slag, fiber, binder, polyvinyl, density

1 Introduction

Blast furnace (BF) slag is the most important by-product of the iron making process, with approximately 220 million tons generated in China annually [1–3]. Currently, BF slag is predominantly treated via water quenching and subsequently utilized to produce low value-added products, such as cement, civil engineering materials, roadbed materials, and concrete admixture [4–6]. However, large amounts of sensible heat in the BF slag cannot be utilized during the water quenching treatment, which would cause considerable wastage of water resources and production of harmful gases such as H2S and SO2 [7–9].

To utilize both BF slag and its sensible heat, a methodology of using BF slag to produce slag fiber was developed [10–12]. As an insulation material demonstrating excellent performance and low cost, BF slag could play a more significant role in many fields such as heat insulation, fire prevention, and noise reduction. In the production process of slag fiber insulation products, binders are commonly used to bond fibers as a whole, where the type of binder determines the fiber adhesion and the bonding strength of the fiber product [13]. Water glass is a kind of inorganic binder that is widely used in industrial production owing to its excellent bonding performance and good heat resistance. However, the disadvantages of water glass as a binder are also apparent, such as poor water and impact resistance and brittleness [14]. Kalel et al. [15] concluded that adjusting the content of phenolic resin as a friction material binder improved some brake-pad properties. Wu et al. [16] also highlighted that phenolic resin is convenient for curing, demonstrating excellent waterproof properties, thermal stability, and aging resistance. However, a large quantity of formaldehyde gas would be released during the production of fiber products when using phenolic resin as the binder.

To obtain an environmentally friendly binder, polyvinyl alcohol (PVA) was considered to be the base binder and modified using glutaraldehyde (GA) in this study for producing fiber insulation pipes. In this study, fiber insulation pipes were prepared using water glass, PVA, and PVA–GA binders. Three main performance indexes – bulk density, mass moisture absorption, and thermal conductivity coefficient (TCC) – were tested to
realize the best possible binder and insulation pipe products.

2 Experiment

2.1 Raw materials

The slag fiber used in the experiment was prepared on the pilot-scale test platform. The fiber was fabricated from molten BF slag, which was directly spun and formed via centrifugal force under the high-speed operation of four roller centrifuges. The residue during the slag fiber preparation was removed by ultrasonic oscillation cleansing, and the fiber was then dried in a blast drying oven at 80°C for 1 h. The average fiber diameter was 4.0–4.8 µm, and the specific composition of the raw materials is presented in Tables 1 and 2.

During the binder preparation, water glass (Na$_2$SiO$_3$) solutions at 4, 6, 8, 10, 12, and 14 wt% were prepared. PVA solutions of 1, 2, 3, 4, 5, and 6 wt% were similarly prepared. PVA–GA solutions were prepared using a mixture of 3 wt% PVA and 1, 2, 2, 3, 4, and 5 wt% GA. The aforementioned three solutions were for use as the binder in the insulation pipe manufacturing process.

2.2 Preparation of thermal insulation pipe

The binder was sprayed during the process of laying the fiber in the pipe molds. The slag fiber was pressed to pipe samples under a pressure of 2,500 N and dried in the blast drying oven for 6 h at 120°C. The slag fiber pipes with different binder additions were subsequently obtained. During this process, uniform binder spraying, rolling pressure, and curing temperature should be ensured as far as possible. The slag fiber pipes samples are shown in Figure 1; specifically, the TCC measurements were conducted using boards with dimensions of 300 mm × 300 mm × 40 mm. The specific plan employed for the preparation of the experimental sample is presented in Table 3. Six samples were prepared for each specific protocol, three of which were used for TCC detection.

2.3 General analytic methods

The bulk density of the insulation pipes was measured and calculated according to the size and the density testing method [17]. The samples were then dried and cooled to room temperature and selected to be weighed, such that the percentage of mass change after continuous weighing was within 0.2%. The bulk density of the insulation pipe is calculated using the following equation:

$$\rho = \frac{4m \times 10^6}{\pi(D^2-d^2)h},$$

where ρ, m, D, d, and h are the bulk density, mass, outer diameter, internal diameter, and length of pipe, respectively.

During measurement of the moisture absorption capacity, the insulation pipes were placed in the maintenance box under adjustable temperature and humidity, which were set to 0 ± 2°C and 95 ± 3%, respectively. After 96 h, the samples were removed and immediately placed in the sample bags for cooling to room temperature. The mass of pipes was measured again, and the moisture absorption capacity of the insulation pipes was obtained using equation (2) [18]:

$$\omega = \frac{m_l - m}{m} \times 100\%,$$

where ω and m$_l$ are the moisture absorption capacity and mass of the pipes, respectively, after moisture absorption. The wetting angle of the fiber pipes was observed using the CA100B measuring instrument.

The TCC was obtained using the im-DRY3001 apparatus. It can be calculated using equation (3) [19]:

$$\lambda = \frac{Q \cdot d}{A \cdot \Delta x \cdot \Delta T},$$

Table 1: Chemical composition content of raw materials/%

| Raw materials  | Al$_2$O$_3$ | SiO$_2$ | MgO  | CaO   | TiO$_2$ |
|----------------|-------------|---------|------|-------|---------|
| BF slag        | 14.62       | 33.95   | 7.84 | 35.02 | 1.02    |
| Iron tailing   | 4.93        | 71.92   | 4.14 | 3.07  | 0.15    |

Table 2: Fiber acidity coefficient and ratio of raw materials.

| Ratio of BF slag (%) | Ratio of iron tailing (%) | Fiber acidity coefficient |
|----------------------|---------------------------|--------------------------|
| 85.4                 | 14.6                      | 1.4                      |
where $\lambda$, $Q$, $A$, $\Delta z$, and $\Delta T$ are the TCC, heat transfer through the sample at steady state, area of the heating plate, measurement interval, and temperature difference between the front and rear of the sample, respectively.

### 3 Results and discussion

#### 3.1 Bulk density of thermal insulation pipes

Bulk density is one of the most important indexes for measuring the thermal insulation pipe quality, which should neither be too low nor too high; this is because an insulation pipe with low bulk density will not achieve the expected insulation effect, significantly wasting the time and the cost invested by the insulation engineering. Conversely, using an insulation pipe with a too high bulk density will cause an increase in raw fiber and binder waste. Therefore, it is particularly necessary to investigate the bulk density of thermal insulation pipes.

Figure 2 shows the bulk density of insulation pipes fabricated using Na$_2$SiO$_3$ and PVA binders. As shown in Figure 2, the bulk density of two kinds of pipes increased with the increase in binder concentration. This indicated that the bulk density of the insulation pipe depends on the binder concentration and dosage under certain conditions of fiber quality, pipe size, and other factors. When the concentration of the water glass was between 4% and 14%, the bulk density of the insulation pipe increased from 156.27 to 187.52 kg/m$^3$. For the pipes fabricated using PVA binder, the bulk density increased from 141.62 to 177.12 kg/m$^3$ in the range of 1–6% PVA binder concentration. The bulk density of the insulation pipes was similar, approximately 156.27 kg/m$^3$, when the PVA and water glass binder concentrations were 3% and 4%, respectively. The aforementioned results show that the bulk density met the Chinese national standard requirements [20].

The adhesive force of PVA arises because of the membrane formed following the loss of solvent during curing. Considering the crosslinking reaction between GA and PVA [21,22], a certain quantity of alcohol hydroxyl can be consumed to form the acetal group, following which a three-dimensional network polymer is formed. In the experiment, the PVA binder was modified using GA. The influence of GA concentration in the PVA–GA binder on the insulation pipe's bulk density was studied under the specific preparation conditions.
Figure 3 shows the bulk density of the insulation pipes prepared using the PVA–GA binder. It can be seen that the bulk density first increased and then significantly decreased with the increase in GA concentration from 0 to 5%. When the concentration of GA increased from 0 to 2%, the actual mass of fiber pipe increased after drying. Although a crosslinking reaction between the PVA and GA molecules also occurred, the bulk density of the fiber pipe increased slightly due to the incomplete reaction. The maximum density was 160.62 kg/m³, with a 2% GA concentration. With the increase in GA concentration, the cross-linking reaction between PVA and GA was more thorough, whereby a higher GA concentration resulted in more efficient cross-linking. The reaction reduced the bulk density of fiber pipes, forming a three-dimensional network polymer during the reaction. When the GA concentration was 5%, the bulk density of the fiber pipe decreased to 145.57 kg/m³. Compared with the pure PVA binder, the crosslinked PVA–GA binder has more advantages concerning the bulk density of fiber pipes.

3.2 Moisture absorption capacity of thermal insulation pipe

Due to the poor working environment of the fiber insulation pipe, there are certain requirements on the pipe shell performance, in particular, water resistance. If the fiber insulation pipe absorbs moisture, it will increase the bulk density of the pipe shell itself. However, it will also increase the number of thermal bridges between the fibers after absorbing water, which will cause a sharp reduction in the slag fiber insulation pipe’s thermal resistance, thus reducing the insulation effect, mechanical strength, and durability of the fiber pipe [23]. Therefore, it is critical to develop an excellent water proof system binder for the development of the fiber insulation pipe. This section describes the measurement of the moisture absorption capacity that was conducted to test the waterproof performance of several binders.
The results obtained on measurement of the moisture absorption capacity of the insulation pipes are presented in Figure 4. One can see that the moisture absorption capacity gradually increased with the increase in PVA and Na₂SiO₃ binder concentration owing to the binder’s high proportion of hydrophilic substance. In comparison, the moisture absorption capacity of the fiber pipe manufactured using PVA was smaller compared to that manufactured using water glass. However, the moisture absorption capacity of slag wool and its products for thermal insulation should be under 5%, as mandated by the GB/T 11835-2007 standard. Consequently, neither PVA nor water glass is suitable for use as a slag fiber pipe binder owing to their poor waterproof properties. PVA modification using GA was also considered. The influence of GA concentration in the PVA–GA binder on the insulation pipe’s moisture absorption was studied under the specific preparation conditions.

Figure 5 shows the moisture absorption capacity of the insulation pipes manufactured using the PVA–GA binder. Figure 5 shows that the moisture absorption capacity significantly decreased with the increase in GA concentration. When the GA concentration was 5%, the moisture absorption capacity was approximately 1.19%, significantly below the standard value. It is known that the crosslinking reaction will occur and a certain amount of alcohol hydroxyl can be consumed to form an acetal group if the PVA and GA are mixed, which leads to the improvement in waterproof performance. Meanwhile, there was a clear enhancement to the stability and the strength of the fiber pipe.

To further study the hydrophobicity of fiber products, the wetting angles of fiber pipes, fabricated using the aforementioned three binders, were measured; a larger wetting angle results in a better waterproof performance of the material. Figure 6 shows the results of the wetting angles of fiber pipes. One can see that the wetting angles were 82.4°, 99.0°, and 118.2°, respectively, indicating that the fiber pipes fabricated using PVA–GA binder had the best waterproof properties, followed by the PVA and water glass binder.

3.3 TCC of the thermal insulation board

TCC is one of the most important parameters in evaluating the thermal insulation effect of different insulation materials. The TCC values of the different samples are shown in Figure 7. It can be seen that these values were significantly influenced by the binder concentration, which was related to the changes in bulk density. The TCC values of the insulation boards fabricated using PVA gradually increased with the increasing PVA concentration. The TCC values increased from 0.0263 to 0.0435 W/(m·K) when the concentration of PVA increased from 3 to 6%. Unlike the TCC values of boards fabricated using the PVA binder, those of
boards fabricated using water glass first decreased and then increased with the increasing water glass concentration. The minimum TCC value was 0.0122 W/(m·K), which indicates the best thermal insulation effect. Thus, it can be concluded that if the Na$_2$SiO$_3$ concentration is too high or too low, the TCC value will increase, which is not conducive to thermal insulation.

The influence of GA concentration on the TCC of insulation boards is shown in Figure 8. Figure 8 shows that the TCC value gradually decreased with the increase in GA concentration. When the PVA and GA were mixed, the TCC of the samples clearly decreased owing to the cross-linking reaction between PVA and GA and the three-dimensional net structure formed; the special structure increased the porosity of the fiber boards and eventually reduced the TCC of the samples. The higher GA concentration results in more complete cross-linking reactions. When the GA concentration was 5%, the lowest TCC was 0.166 W/(m·K).

4 Conclusions

In this study, BF slag fiber pipes were prepared to investigate the influence of PVA–GA binders on the properties of the samples. Three main performance indexes, namely, bulk density, mass moisture absorption, and TCC, were measured and compared among samples fabricated using water glass, PVA, and PVA–GA binders. On the basis of the experiment results, the following conclusions can be drawn:

1. Under the same rolling pressure, volume conditions, and frequently used binder concentration range, the average bulk density of the samples prepared using PVA is lower than that of the samples prepared using Na$_2$SiO$_3$. When PVA is modified using GA, the bulk density of the samples further decreases along with their absorption capacity.

2. For the samples prepared using Na$_2$SiO$_3$ and PVA, the moisture absorption capacity increases with the increase in binder concentration, and the samples prepared using Na$_2$SiO$_3$ absorb water more effectively. However, the moisture absorption capacity of the samples is reduced by the mixture of GA and PVA; therefore, the waterproof performance of the samples prepared using PVA–GA is better.

3. By comparative analysis, the PVA–GA binder can not only ensure a better bulk density and waterproof properties of the slag fiber products but also maintain the same level of thermal insulation performance as other binders. Furthermore, the experiment demonstrated that best binder composition is PVA–GA, prepared using 3 wt% PVA and 5 wt% GA.

In the future, the most environmentally friendly binder will be found and developed via composition optimization.

References

[1] Murthy, I. N., and J. B. Rao. Granulated blast furnace slag: potential sustainable material for foundry applications. *Journal of Sustainable Metallurgy*, Vol. 3, 2017, pp. 495–514.
[2] Wu, J. J., H. Wang, X. Zhu, Q. Liao, and B. Ding. Centrifugal granulation performance of liquid with various viscosities for heat recovery of blast furnace slag. *Applied Thermal Engineering*, Vol. 89, 2015, pp. 494–504.

[3] Zhu, X., H. Zhang, Y. Tan, H. Wang, and Q. Liao. Analogue experimental study on centrifugal-air blast granulation for molten slag. *Applied Thermal Engineering*, Vol. 88, 2015, pp. 157–164.

[4] Song, K., S. Park, W. Kim, C. W. Jeon, and J. W. Ahn. Effects of experimental parameters on the extraction of silica and carbonation of blast furnace slag at atmospheric pressure in low-concentration acetic acid. *Metals*, Vol. 199, 2017, pp. 1–14.

[5] Nidheesh, P. V., and M. S. Kumar. An overview of environmental sustainability in cement and steel production. *Journal of Cleaner Production*, 2019.

[6] Kelly, O., D. Aveline, B. Farid, and G. Richard. Early-age self-healing of cementitious materials containing ground granulated blast-furnace slag under water curing. *Journal of Advanced Concrete Technology*, Vol. 14, 2016, pp. 717–727.

[7] Huang, W. Steel industry "12th five-year" development plan mid-term review. *China Steel Focus*, Vol. 26, 2013, pp. 4–11.

[8] Zhao, Y., D. F. Chen, Y. Y. Bi, and M. Long. Preparation of low cost glass-ceramics from molten blast furnace slag. *Ceramics International*, Vol. 38, 2012, pp. 2495–2500.

[9] Samet, B., and M. Chaabouni. Characterization of the Tunisian blast-furnace slag and its application in the performance of a cement. *Cement & Concrete Research*, Vol. 34, 2004, pp. 1153–1159.

[10] Yabuta, K., H. Tozawa, and T. Takahashi. New applications of iron and steelmaking slag contributing to a recycling-oriented society. *JFE Technology*, Vol. 10, 2006, pp. 17–23.

[11] Xiao, Y. L., Y. Liu, and Y. Q. Li. Status and development of mineral wool made from molten blast furnace slag. *Baosteel Technical Research*, Vol. 5, 2011, pp. 3–8.

[12] Zhang, Y. Z., W. X. Liu, W. Zhang, H. W. Xing, and J. Li. Experimental research of producing slag wool with modified blast furnace slag as raw materials. *Journal of Functional Materials*, Vol. 43, 2012, pp. 59–62.

[13] Zhang, H. *Study on modification and application of mineral cotton fiber*. East China University of Science and Technology, Shanghai, 2013.

[14] He, X. X., C. D. Yan, and Z. G. Sun. *Inorganic adhesive*. Chemical Industry Press, Beijing, 2013, pp. 1–2.

[15] Kalel, N., J. Bijwe, and A. Darpe. Influence of amount of phenolic resin on the tribological performance of environment-friendly friction materials. *SAE Technical Paper*, 2019.

[16] Wu, H. D., P. P. Chu, and C. C. M. Ma. Thermodynamic properties of the novolac type phenolic resin blended with poly(hydroxyl ether of bisphenol A). *Polymer*, Vol. 39, 1998, pp. 703–709.

[17] GB/T5480-2008. Test methods for mineral wool and its products. 2008.

[18] Kang, Y., Y. Z. Zhang, C. Liu, and M. F. Jiang. Study on mix proportion of new binder of blast furnace slag wool insulation board. *New Building Material*, Vol. 7, 2017, pp. 89–92.

[19] Zhang, Z. Q., Y. Z. Zhang, A. M. Yang, H. W. Xing, T. L. Tian, and Z. H. Li. Preparation and properties of slag wool board using modified polyvinyl alcohol as binder. *Materials and Manufacturing Processes*, Vol. 31, 2016, pp. 168–172.

[20] GB/T11835-2007. Rock wool, slag wool and its products for thermal insulation. 2007.

[21] Zhu, H. Y., and L. Xiao. Influence of moist heat treatment or cross linking on the water resistance properties and structure of Chitosan/PVA blend films. *Journal of Zhejiang Ocean University (Natural Science)*, Vol. 24, 2005, pp. 126–129.

[22] Kang, Y. Performance optimization of insulation board from blast furnace slag fiber. Master’s thesis. North China University of Science and Technology, 2016.

[23] Zhao, Z. N. *Heat transfer*. Higher Education Press, Beijing, Vol. 2, 2002, pp. 54–69.