Optimal type and ratio of foaming agent, foaming stabilizer and fluxing agent of foam glass fabricated with red mud and coal gangue

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In order to effectively reuse red mud and coal gangue, foam glass was successfully prepared by sintering. The foaming of foam glass is ensured by adding foaming agent, foam stabilizer and fluxing agent to the raw materials including red mud, coal gangue and waste glass. Furthermore, the defects in the foam glass are also reduced. The obtained powder was dried at 105 ºC and characterized by XRF, DSC-TG analysis, etc. According to cellular structure, apparent density and water absorption, the optimal type and ratio of foaming agent, foaming stabilizer and fluxing agent were revealed. The results indicate that the optimized formula of foaming agent, foaming stabilizer and fluxing agent is 3% MnO_2-2% Na_3PO_4-2% borax. The foam glass prepared under optimized conditions exhibits uniform porous distribution and suitable pore size with an apparent density of 0.575 g/cm^3 and water absorption of 4.61%. The research in this work could establish the technical foundation of red mud-based porous material for industrial production.

Keywords: Foam glass, Foaming agent, Foaming stabilizer, Fluxing agent, Optimal type and ratio.

Introduction

Red mud has been the major solid wastes of Bayer process of alumina extraction from bauxite, while the annual production of red mud reaches 50 to 80 million tons in the global world [1]. Researchers have made many efforts to recycle the red mud in different fields, such as cement, sintered brick, ceramsite, adsorbent materials and extraction of noble metal. However, the utilization of red mud owing to its relatively high alkali content is still a worldwide problem and thus largely restricts its potential application [2-7]. Coal gangue is one of the solid wastes in the process of coal mining and washing. The amount produced in China is reached above several million tonnes and increases by about one million tonnes per year [8]. Although it has been reused in the fields of cement and concrete, etc., the utilization ratio is still comparatively low compared to the high generation of 1.3 billion tons every year [9-11]. The disposal of waste glass has also become a global environmental problem. It amounts to about 2–8% in urban waste [12], and the amounts of generation reach up to 7.5 million tons every year in China. However, due to the low recovery rate of 25%–30%, most solid wastes can only be placed in the open air. Therefore, it is of great importance to find a suitable way to recycle red mud, coal gangue and waste glass.

As the demand for energy saving and environmental-friendly products is increasing, foam glass has been applied in the fields of green construction, fire prevention and thermal insulation due to the dramatic feathers of anti-corrosion and thermostability. During the past decades, foam glass prepared by solid wastes, such as tailings, sludge, etc., have been widely studied [13-16]. Using solid waste in foam glass production is for the consideration of protecting environment and reducing the production cost of foam glass because it expands the range of choices for raw materials. It leads to a new trend in commercialized production of glass foams [17]. To our knowledge, coupling red mud with coal gangue to prepare foam glass has not yet largely studied. Furthermore, red mud and coal gangue is rich in SiO_2, CaO and Al_2O_3, which is the basic composition of foam glass [18, 19]. In addition, it is beneficial to reduce the sintering temperature and cut the cost due to the high content of alkali metal elements in the red mud, which is consistent with the findings of D. S. Jung et al., who found the glass transition temperature was deceased from 517.3 ºC to 468 ºC when the amount of Na_2O added to the product was changed from 0 to 5.7 wt.% [20]. Thus, it is a feasible way to prepare foam glass with the red mud, coal gangue and waste glass, and provides an important means to recycle red mud, coal gangue and waste glass scrap as well. However, considering the prepared foam glass with a low quality, it is necessary to investigate the proper type and ratio of foaming agent, foaming stabilizer and

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Table 1. Chemical composition of red mud, coal gangue and waste glass (*wt*/%)

Compositions	SiO₂	CaO	Al₂O₃	MgO	Fe₂O₃	K₂O+Na₂O
Red mud	20.92	17.79	28.30	1.84	12.98	10.30
Coal gangue	60.62	2.27	25.56	0.97	4.97	2.99
Waste glass	66.03	11.39	2.63	1.71	1.25	14.42

fluxing agent to accommodate with the material system and sintering temperature.

In this study, the red mud, coal gangue and waste glass were selected as the raw materials to prepare the foam glass. The types and contents of admixtures on cellular structure, apparent density and water absorption were investigated systematically. Meanwhile, the technological parameters were well optimized. The research in this work could establish the foundation for preparing foam glass with solid wastes.

Experimental Materials and Methodology

Materials

Red mud, coal gangue and waste glass were purchased from Henan shenhuo new materials Co. Ltd. Calcium carbonate ($CaCO_3$), manganese dioxide (MnO_2), sodium silicate ($Na_2SiO_3 \cdot 9H_2O$), trisodium phosphate (Na_3PO_4),

Table 2. Raw materials formula and additive design of foaming agent for foam glass (*wt*/%)

Waste glass	Red mud	Coal gangue	Trisodium phosphate	Borax	Foaming agent
40	21.90	38.10	2	2	2
40	21.90	38.10	2	2	3
40	21.90	38.10	2	2	4
40	21.90	38.10	2	2	5
40	21.90	38.10	2	2	6

Table 3. Raw materials formula and additive design of foam stabilizer for foam glass (*wt*/%)

Waste glass	Red mud	Coal gangue	Calcium carbonate	Borax	Foam stabilizer
40	21.90	38.10	3	2	1
40	21.90	38.10	3	2	2
40	21.90	38.10	3	2	3
40	21.90	38.10	3	2	4
40	21.90	38.10	3	2	5

Table 4. Raw materials formula and additive design of fluxing agent for foam glass (*wt*/%)

Waste glass	Red mud	Coal gangue	Calcium carbonate	Trisodium phosphate	Fluxing agent
40	21.90	38.10	3	2	1
40	21.90	38.10	3	2	2
40	21.90	38.10	3	2	3
40	21.90	38.10	3	2	4
40	21.90	38.10	3	2	5

sodium carbonate (Na_2CO_3), borax and boracic acid were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. All chemicals were analytical grade and used as received without further purification. The composition of red mud, coal gangue and waste glass were shown in Table 1.

Experiment design

The amounts of foaming agent, foaming stabilizer and fluxing agent were shown in Table 2, 3 and 4, respectively.

Preparation of foam glass

The samples were prepared as follows. The red mud, coal gangue and waste glass are grinded into powder respectively and screened through a 180-mesh sieve. Then, the red mud, coal gangue, waste glass, foaming agent, foam stabilizing agent and flux are evenly mixed according to the design content of the formula. After aging process of 48 hours, the green body was obtained by pressed in mould and dried at 105 °C inside the drying oven. Finally, the dried green body was put into the resistance furnace for high temperature sintering, and the foam glass was prepared.

The DSC-TG spectra of the sample was shown in Fig. 1. According to the results of DSC-TG spectra, the preparation process of foam glass was illustrated in Fig. 2. The first stage (ABC, preheating), the green body was heated to 500 °C at a rate of 10 °C min⁻¹ and maintained at 500 °C for 30 minutes. The second stage (CDE, foaming), the sample was heated to 950 °C and maintained at this temperature for 30 min. The third stage (EF, foam stabilization), the cellular structure was formed at this stage. The last stage (FG, annealing),
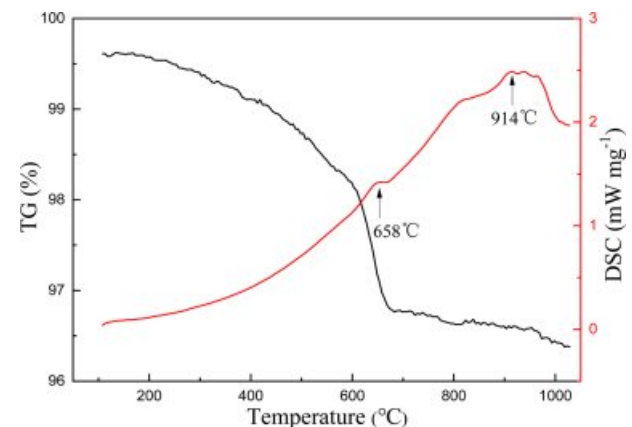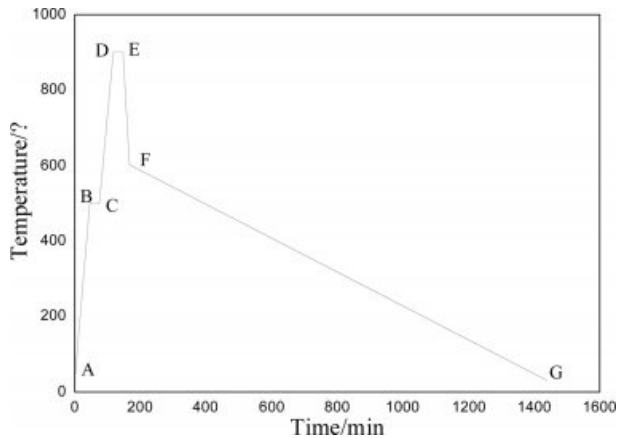

Fig. 1. DSC/TG curves of sample.

Fig. 2. The sintering process of foam glass.

cooling to room temperature within the furnace, the internal stress of foam glass was eliminated gradually to avoid the appearance of cracks.

Characterization of the foam glass

The chemical compositions of red mud, coal gangue and waste glass were measured by X-ray fluorescence spectroscopy (XRF), and the cellular structure of foamed glass was observed by using camera. The DTA-TG analysis of samples was carried out by the DSC/TG (Netzsch STA449F3, German). The apparent density was measured according to the Archimedes principle : $F = \rho g v$, F: buoyance, ρ: density of H_2O, g: acceleration of gravity, v: volume of drained water. Water absorption can be calculated based on the equation: $W_m = (m_2 - m_1)/m_1$, W_m: water absorption, m_1: the mass of material in dry condition, m_2: the quality of material in saturated state of water absorption.

Results and Discussion

The influence of foaming agent on cellular structure and properties of foam glass

   The influence of foaming agent on cellular structure

   The digital images of foam glass with different foaming agent and the adding amount were illustrated in Fig. 3. It can be seen that the type and amount of foaming agent showed a significant impact on the cellular structure. For $CaCO_3$, the pore size of honeycomb hole becomes larger gradually and the wall got thinner along with increasing the contents. The products showed a thick pore wall and low porosity with lower content of $CaCO_3$. However, if the mass fraction of $CaCO_3$ was increased by more than 4%, the pore coalescence emerged and cellular structure has been broken as depicted in Fig. 3(a). For $Na_2SiO_3 9H_2O$, the generated cellular structure was irregular with serious pore coalescence (as shown in Fig. 3(b)). For MnO_2, As shown in Fig. 3(c), the foaming process was fully achieved with a uniform pore size and thin pore wall.
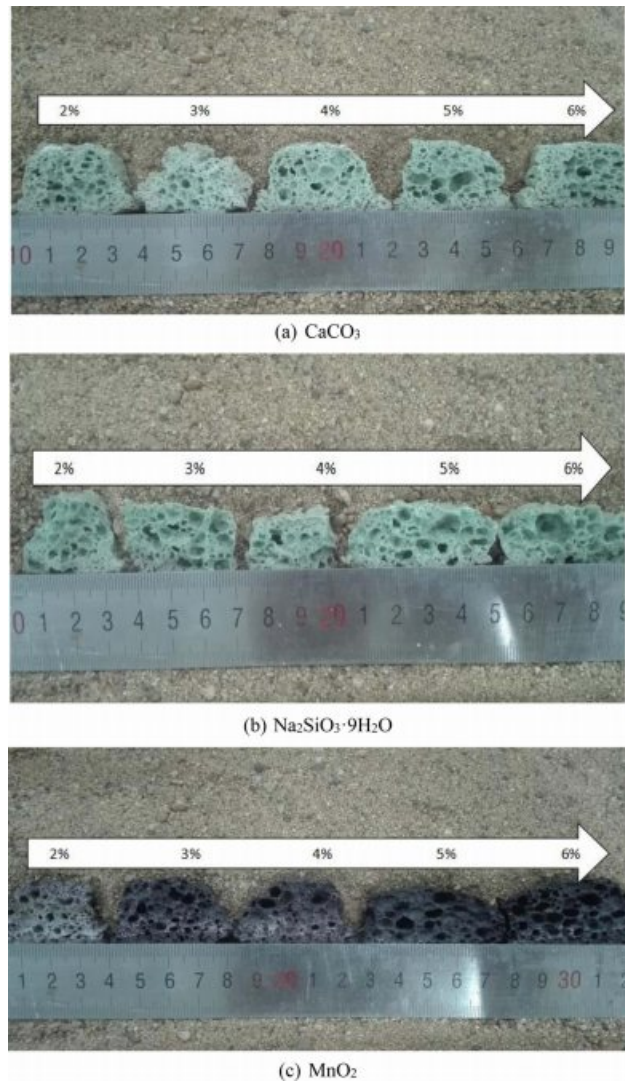

Fig. 3. The effect of the type and amount of foaming agent on the cellular structure of foam glass.

Similarly, if the mass fraction of MnO_2 was enlarged more than 3%, the pore coalescence appeared. Based on the above analysis, the mechanism can be illustrated as below: with the increasing addition of foaming agent, gas was generated from the decomposition of foaming agent, leading to increased internal pressure and formation of connectivity pore. This agrees well with the findings of N. Chen et al., who found when the content of foaming agent was too small, it was difficult to mix glass powder and foaming agent evenly, resulting in uneven distribution of pores. And excessive content of foaming agent can cause the accumulation of small pores to form large holes, leading to non-uniformity of pore size and bad foaming quality [12].

   The influence of foaming agent on apparent density

   The apparent density of foam glass with different foaming agent and the adding amount were shown in

Fig. 4. It can be noted that the apparent density of foam glass decreased along with increasing the contents of foaming agent, especially for the $CaCO_3$ and MnO_2. Nevertheless, for $Na_2SiO_3 9H_2O$, the foam glass exhibited a higher apparent density with a much slower tendency of decline comparing to other two foaming agents. Moreover, the apparent density of sample obtained with $Na_2SiO_3 9H_2O$ was almost 1.6 times higher than that with the MnO_2 when the addition was up to 5%. These results were quite agreed with the features of cellular structure shown in Fig. 3. In general, the foaming performance of samples with $CaCO_3$ or MnO_2 was better than that with $Na_2SiO_3 9H_2O$ due to the lower apparent density.

The influence of foaming agent on water absorption

The water absorption of foam glass with different foaming agent and the adding amount were shown in Fig. 5. It should be noted that the water absorption of foam glass increased with increasing the contents of foaming agent, especially for the samples with $CaCO_3$
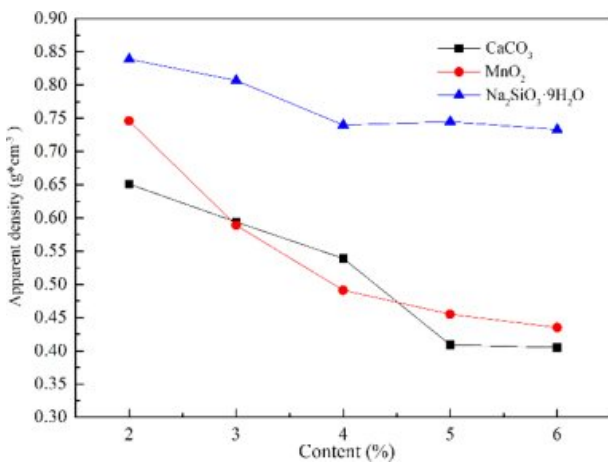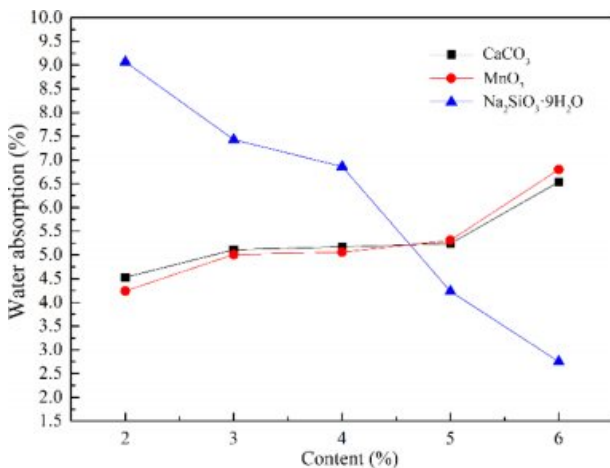
or MnO_2. When the $CaCO_3$ or MnO_2 was added no more than 5%, the water absorption increased slowly. Furthermore, the water absorption of the samples with $CaCO_3$ or MnO_2 increased significantly with an addition of more than 5%. This result indicated that the increased water absorption came from the microporous and interconnecting pores, resulting from the gas decomposed from the foaming agent and the risen internal pressure. While the $Na_2SiO_3 9H_2O$ was chosen as the foaming agent, it exhibited a reverse tendency that the water absorption declined with increasing the contents of $Na_2SiO_3 9H_2O$. From these considerations we concluded that $Na_2SiO_3 9H_2O$ was not matched well with the material system, leading to the gas releasing from glass melt. This was agreed with foregoing influences of foaming agent on cellular structure and apparent density of foam glass. Based on the above results, MnO_2 was selected as the foaming agent and the optimized mass fraction was about 2-3%.

The influence of foaming stabilizer on cellular structure and properties of foam glass

The influence of foaming stabilizer on cellular structure

The digital images of foam glass with different foaming stabilizer and the adding amount were exhibited in Fig. 6. It can be seen that the addition of Na_2CO_3 caused the accumulation of small pores to form large or connected holes, while Na_3PO_4 led to an even distribution of pores when its content was appropriate. By increasing the contents of Na_2CO_3, the pore coalescence emerged seriously. Besides, peeling and blocking appeared

Fig. 4. The effect of the type and amount of foaming agent on the apparent density of foam glass.

Fig. 5. The effect of the type and amount of foaming agent on the water absorption of foam glass.
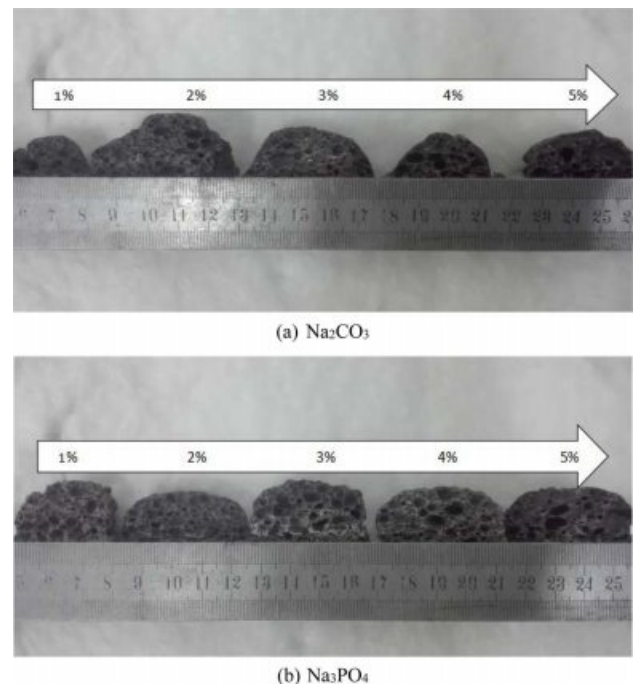

(a) Na_2CO_3

(b) Na_3PO_4

Fig. 6. The effect of the type and amount of foaming stabilizer on the cellular structure of foam glass.

on the surface of samples (as shown in Fig. 6(a)). For Na_3PO_4, if there was a low content in the mixture, it showed a quite good effect of foamstabilization. A typical 2 mm-hole was clearly identified, which was assigned to the mass fraction of 2% of Na_3PO_4. However, if the Na_3PO_4 was added more than 4%, pore coalescence emerged, resulting to the formation of connectivity pore (as shown in Fig. 6(b)). Based on the above analysis, the addition of Na_3PO_4 showed enhanced foamstabilization effect compared to that of the Na_2CO_3.

The influence of foaming stabilizer on apparent density

The apparent density of foam glass with different foaming stabilizer and the adding amount were shown in Fig. 7. It was found that the apparent density of foam glass decreased by increasing the contents of foaming stabilizer of Na_2CO_3 or Na_3PO_4. For a same addition of Na_2CO_3 or Na_3PO_4, the samples with Na_2CO_3 exhibited a lower apparent density than that with Na_3PO_4. It can be analyzed that when the Na_3PO_4 was selected as foaming stabilizer, the surface tension reduced and most of the gas run away, leading to a higher apparent density. For Na_2CO_3, based on the synergistic contribution of gas escaping and fluxing effect, the apparent density of the sample decreased remarkably with increasing the content of Na_2CO_3. This indicates that Na_2CO_3 as the foaming stabilizer caused the accumulation of small pores to form large or connected holes, thus decreasing the apparent density significantly.

The influence of foaming stabilizer on water absorption

The water absorption of foam glass with different foaming stabilizer and the adding amount were shown in Fig. 8. This result implied that the water absorption of foam glass increased with increasing the content of Na_2CO_3. While the Na_3PO_4 was chosen as the foaming stabilizer, it exhibited a reverse tendency that the water
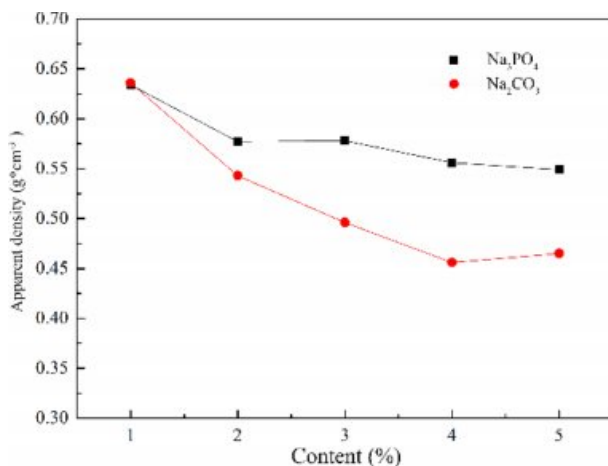
absorption decreased with increasing content of Na_3PO_4. This result indicated that the increased water absorption of sample with Na_2CO_3 obtained originating from the formation of pore coalescence and interconnecting pores, which was benefit for water to flow in the pores of foam glass. From these considerations we indicated that Na_3PO_4 showed well matching with the material system. Based on the above results, Na_3PO_4 was selected as the foaming stabilizer and the optimized mass fraction was about 2–3% with a low water absorption of 4.8%.

The influence of fluxing agent on cellular structure and properties of foam glass

The influence of fluxing agent on cellular structure

The digital images of foam glass with different fluxing agent and the adding amount were shown in Fig. 9. There was a big difference on fluxing effect between borax and boracic acid. The pore size of foam glass got bigger with increasing the content of borax. As shown in Fig. 3(a), a typical 2-3 mm honeycomb hole can be noted, which was assigned to the mass fraction of 2% of borax. However, if the borax was added more than 3%, pore coalescence emerged, leading to the irregular pore structure. Compared to borax, the pore coalescence emerged seriously along with the increasing content of boracic acid. This observation suggested that boracic acid was not matched well with the material system.

The influence of fluxing agent on apparent density

The apparent density of foam glass with different fluxing agent and the adding amount were shown in Fig. 10. It was obviously observed that the apparent density of foam glass dropped by increasing the content of fluxing agent. For a same addition of borax and boracic acid, the sample with borax exhibited a lower apparent density than that with boracic acid. These results were quite agreed with the features of cellular structure shown in Fig. 9. Based on the above results,
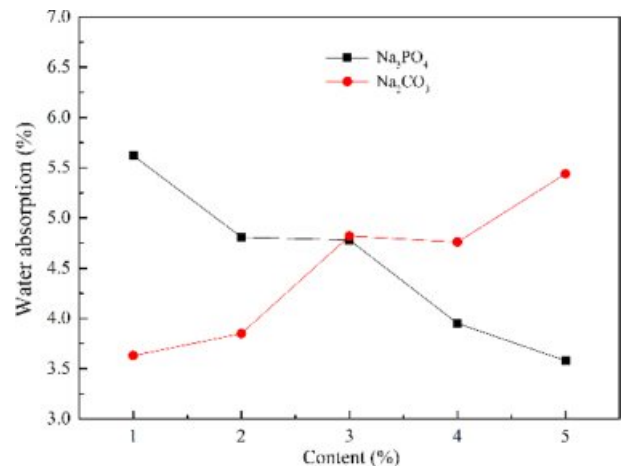

Fig. 7. The effect of the type and amount of foaming stabilizer on the apparent density of foam glass.

Fig. 8. The effect of the type and amount of foaming stabilizer on the water absorption of foam glass.
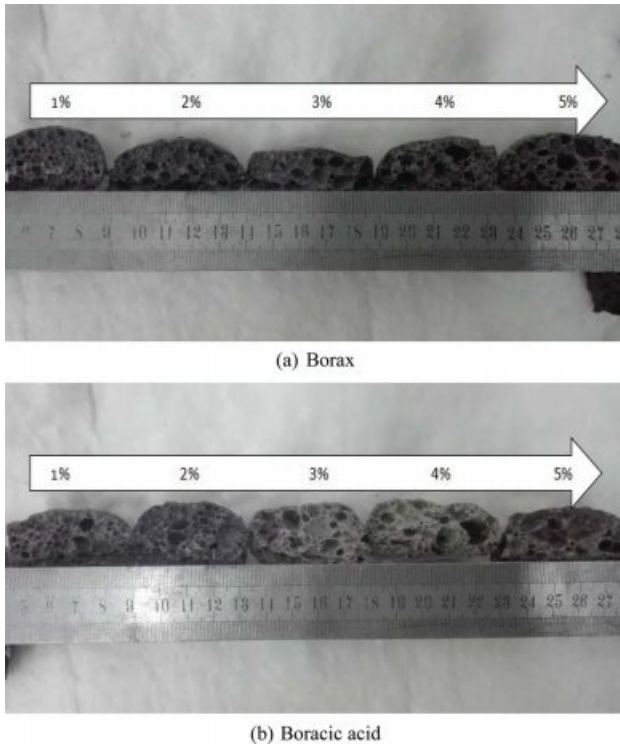
(a) Borax

(b) Boracic acid

Fig. 9. The effect of the type and amount of fluxing agent on the cellular structure of foam glass.
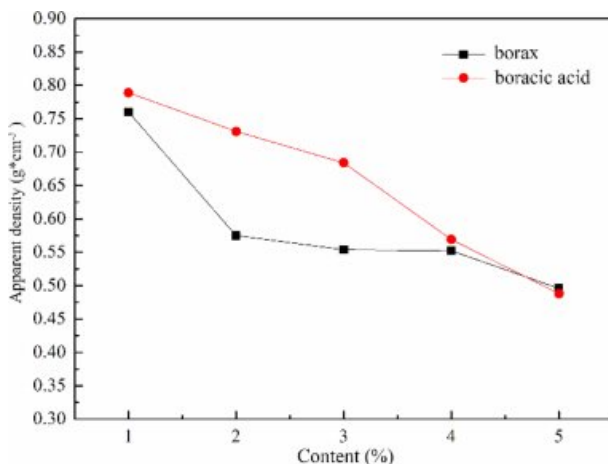

Fig. 10. The effect of the type and amount of fluxing agent on the apparent density of foam glass.

borax was selected as the fluxing agent and the optimized mass fraction was about 2% with an apparent density of 0.575 g/cm^3.

The influence of fluxing agent on water absorption

The water absorption of foam glass with different fluxing agent and the adding amount were shown in Fig. 11. The water absorption of foam glass increased with increasing the content of fluxing agent. For a same addition of borax and boracic acid, the sample with borax exhibited a lower water absorption than that with boracic acid. Under the same foaming tempera-
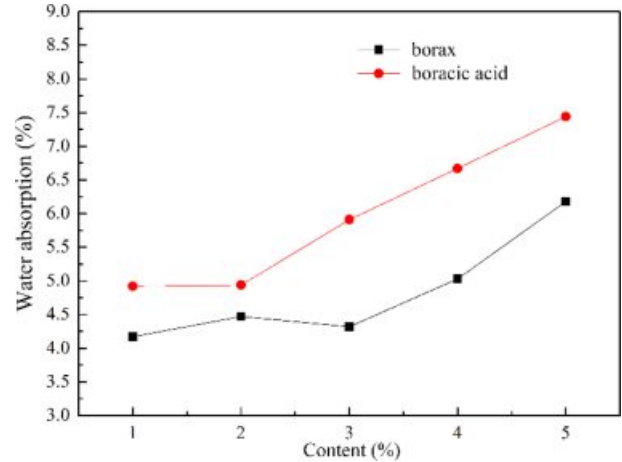

Fig. 11. The effect of the type and amount of fluxing agent on the water absorption of foam glass.

ture, the viscosity of melting glass with fluxing agent can be significantly reduced compared to that without fluxing agent. This was favor for the gas to be generated, which induced to form the pore coalescence and increased the water absorption. From the analysis we considered that borax showed well matching with the material system and the optimized content was about 2% with a water absorption of 4.61%.

Conclusion

In this study, optimal type and ratio of foaming agent, foaming stabilizer and fluxing agent of foam glass with red mud and coal gangue were investigated, the following conclusions were drawn:

(1) The type and amount of foaming agent show a significant impact on the cellular structure, and MnO_2 is selected as the foaming agent and the optimized mass fraction is about 2-3%.

(2) The addition of Na_2CO_3 causes the accumulation of small pores to form large or connected holes, while Na_3PO_4 leads to an even distribution of pores when its content is appropriate at 2%. Thus, Na_3PO_4 as the foaming stabilizer is chosen.

(3) The borax shows well matching with the material system and the optimized content is about 2%, at this time, a typical 2-3 mm honeycomb hole can be noted.

(4) Under the optimized addition of 3% MnO_2-2% Na_3PO_4–2% borax, the prepared foam glass exhibits good performance with an apparent density of 0.575 g/cm^3 and water absorption of 4.61%. Meanwhile, the obtained products showed uniform macroporous structure by introducing the admixtures in the precursor. Systematic studies clearly reveal that the dramatic foaming effect is ascribed to MnO_2 and borax is matched well with the material system.

(5) According to the experimental and analyzed results, this study offers brand new idea to discover property and process parameters, which may conduce

to a better grasp of sustainable applications for solid wastes.

Acknowledgments

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