Preparation and characterization of red mud based porous materials

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Abstract. China was a large country in bauxite mining and refining. One ton of alumina was produced, accompanied by 0.5 ~ 2 tons of red mud [1]. Therefore, the accumulation and pollution of red mud had been a difficult problem to be solved by enterprises and local governments. In this paper, red mud based porous materials were prepared with Bayer red mud, perlite, silicon carbide (as foaming agent) and glass powder (as flux). The effects of sintering process and iron oxide on thermal conductivity, bulk density, porosity and compressive strength of red mud based porous materials were studied by TG-DSC, XRD, SEM and XEDS. The results show that red mud based porous materials with uniform pore distribution could be obtained when the amount of red mud was 60%, perlite was 37%, SiC was 1%, glass powder was 2%, sintering temperature was 1150 ℃ and holding time was 120 min. The true porosity of the red mud based porous material was 70%, and the average pore diameter was 216.84 μ m. The thermal conductivity was 0.26w / (m • K) and the compressive strength was 2.31MPa.

1. Introduction

Red mud is a solid waste discharged from alumina industry. According to different alumina production processes, red mud can be divided into Bayer red mud (BRM), sintering red mud (SRM) and combined red mud (CRM). Red mud was a strongly alkaline solid waste containing a small amount of heavy metals (Liu et al.,2009), and pollution was caused by infiltration of alkaline substances and heavy metals under red mud landfills or transportation pipelines. To solve this problem, resource utilization of red mud had become a significant issue in the area where alumina enterprises were located, and it was also a research hotspot in the field of ecological environment.

Presently, most alumina industries in Shandong Province mainly used Bayer process to produce alumina, so the existing amount of BRM was the largest compared with SRM and CRM. Based on this, BRM was mainly used as the main raw material in this research. The main chemical components of BRM include Fe₂O₃, SiO₂ and Al₂O₃. Different treatment methods of bauxite made the iron oxide content in BRM fluctuate greatly. Currently, researchers had developed a great many of researches about the utilization of red mud resources, such as the preparation of building materials, catalysts, ceramics, modified soil and so on.

Recently, the preparation of porous materials with red mud had attracted extensive attention of environmental protection departments and researchers. Porous thermal insulation materials were prepared with red mud as raw material and carbon dust as pore forming agent. The effects of sintering temperature and pore forming agent content on the structure and properties of porous materials were also studied (Wang et al.,2020). A lightweight thermal insulation porous material was prepared with BRM and glass powder as raw materials, potassium feldspar as flux and polystyrene as foaming agent.
The effects of different batches of red mud on the properties of the materials were studied (Wei et al., 2017). The porous material of thermal insulation decorative brick was prepared by mixing a large amount of red mud with construction waste, polished brick waste and clay. The effects of red mud content on its bulk density, porosity, compressive strength, thermal conductivity and softening temperature were analyzed (Wang et al., 2017). In the existing reports of red mud porous materials, there were more studies on the pore forming mechanism of organic matter (OM) and the influence of sintering temperature on the samples, while there were few studies on the foaming mechanism of silicon carbide and the influence of iron oxide content on the samples. Owing to the fluctuation of iron oxide in BRM, and iron oxide had high density (5~5.25 g/cm³) and high melting point (1565°C), so it might affect the thermal conductivity of red mud based samples. It was significant to study its effect on the thermal properties of red mud porous materials.

In this paper, different sintering processes (1130°C~1160°C, 30min~150min) and different BRM content (60%~65%) were set up. The porosity, bulk density, thermal properties and compressive strength of samples were analyzed, the pore forming mechanism of porous materials was also discussed.

2. Experiment

2.1 Raw materials
Bayer red mud from a local aluminum company, Perlite (SiO2 ≥ 72.5%) produced in Zibo, Silicon carbide powder produced in Zibo and Glass powder (average particle size 325 meshes) made from waste plate glass (SiO2 ≥ 70%) were used in this experiment. The chemical compositions (XRF), mineral phases (XRD) and SEM photos of Bayer red mud were shown in Table 1., Figure 1. and Figure 2. respectively.

Table 1. Chemical compositions of Bayer red mud. wt/\%  
| Component   | Fe2O3 | Al2O3 | SiO2 | Na2O | TiO2 | CaO | Other |
|-------------|-------|-------|------|------|------|-----|-------|
| Content     | 36.1  | 23.2  | 18.4 | 13.4 | 5.03 | 2.28| 1.59  |

Figure 1. SEM of Bayer red mud.  
Figure 2. XRD of Bayer red mud.

Figure 1, showed the morphology of Bayer red mud was agglomerated with fine particles, and the size of the aggregates was about 2~20 μm. There was no obvious cementation between the fine particles that constituted the aggregate and most of them are loose. Figure 2, verified that the Bayer red mud mainly contained nepheline (NaAlSiO4), forsterite (Ca2SiO4), mullite (3Al2O3·2SiO2), chlorite [Na0.5Al6Si8O20(OH)10·H2O], sodium metasilicate pentahydrate (Na2SiO3·5H2O), goethite (Fe2O3·H2O), hematite (Fe2O3) and calcite (CaCO3).

2.2 Experimental methods
The red mud, perlite, SiC and glass powder were mixed according to the compositions shown in Table 2.
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Table 2. Raw material formula table.

| Number | Red mud | Perlite | SiC | Glass powder |
|--------|---------|---------|-----|--------------|
| C0     | 60      | 37      | 1   | 2            |
| C1     | 62      | 35      | 1   | 2            |
| C2     | 64      | 33      | 1   | 2            |
| C3     | 65      | 32      | 1   | 2            |

2.2.1 Sample preparation
Red mud and various additives were weighed in proportion to make mixed powder. The mixed powder was put in the ball crusher to make the mixture well-distributed. After mixing, the mixture was put in 125 mm ×105 mm ×68 mm crucible and was compacted. Then different sintering temperature (1130~1160℃) were predestined and the energy-saving box type electric furnace at the rate of 3℃/min to heat the predetermined temperature was used. Subsequently, different holding time (30~150min) were set. Finally, the sample was cooled naturally for saving and testing.

2.2.2 Characterizations
The compressive strength was measured by universal mechanics testing machine (Instron 5969) in triplicate. The thermal conductivity was tested by thermal conductivity meter (Tc-3200) with transient hot wire method. The true porosity and bulk density were measured with static weighing method and Archimedes principle. The microstructure was observed by field emission scanning electron microscope (Quanta 250). The phase component was determined by Bruker X-ray diffractometer (AXS-D8-02). The composition of red mud was detected by ZSX 100e. The raw material and mixture of red mud were analyzed by using comprehensive thermal analyzer (SDT650).

3. Results and discussion

3.1 Temperature and time

3.1.1 TG-DSC

As shown in Figure 3a., the first temperature range was 80℃~200℃. Dehydration of chlorite [Na0.5Al6Si8O20(OH)10•H2O], sodium metasilicate pentahydrate (Na2SiO3•5H2O) and goethite (Fe2O3•H2O) in BRM resulted in weight loss. The second region was 200℃~400℃ with 7.798% of weight loss and it had an endothermic peak which was due to the dehydration of chlorite [Na0.5Al6Si8O20(OH)10•H2O].
(OH)$_{10}$$\cdot$H$_2$O, sodium metasilicate pentahydrate (Na$_2$SiO$_3$$\cdot$5H$_2$O) and goethite (Fe$_2$O$_3$$\cdot$H$_2$O). The third range was at 400℃ ~ 600℃ with 1.082% weight loss, and there was a small endothermic peak. Figure 2. showed that it was caused by the decomposition of a small amount of aragonite [Ca (CO$_3$)]. The fourth region was at 600℃ ~ 800℃ with 0.53% weight loss, there was no obvious heat absorption peak and exothermic peak in this interval. In this temperature range, the less mass loss was due to the complete reaction of volatile and decomposable components in Bayer red mud.

Figure 3b. verified that the weight loss of mixed powder was same as Bayer red mud before 600℃. The difference was that the loss amount of mixed powder was 0.239% and accompanied by exothermic peak at 600℃ ~ 800℃, it was because the melting of glass powder promotes the reaction of SiC and oxygen to produce carbon monoxide. At 950℃ ~ 1100℃, the weight loss rate of C0 mixture was 0.223%. The exothermic peak in this temperature range was due to the continuous melting of perlite, which further promoted the reaction between SiC and oxygen.

Bayer red mud contained iron oxide and amorphous silicate. The main composition of perlite was SiO$_2$. Perlite gradually melted when the temperature exceeded 1000℃, while glass powder began to melt above 600℃. Therefore, an appropriate amount of glass powder and perlite could expand the melting temperature range to 600 ~ 1100℃. In the environment of high temperature and containing silicate melt, SiC reacted easily with oxygen to generate CO and CO$_2$. These gasses generated by the reaction form bubbles in the high-temperature melt so as to play the role of foaming. The reaction equation and Gibbs free energy of SiC and O$_2$ at 298.15K are as follows [6-7].

\[
\begin{align*}
\text{SiC} (s) + O_2 (g) & \rightarrow \text{SiO}_2 (g) + CO (g) = -193\text{KJ/mol} \quad (1) \\
\text{SiC} (s) + 2O_2 (g) & \rightarrow \text{SiO}_2 (g) + CO_2 (g) = -1178\text{KJ/mol} \quad (2)
\end{align*}
\]

According to the theory of thermodynamics, the reaction could happen spontaneously when its Gibbs free energy was less than zero. SiC was oxidized to dense SiO$_2$ film at medium temperature. There were a lot of alkaline oxides in Bayer red mud, such as K$_2$O, Na$_2$O, MgO, CaO, etc. With the increased of temperature, alkaline oxides melt would destroy the SiO$_2$ film and generated more silicate liquid phase, which promoted the penetration of oxygen. Thus SiC reacted with O$_2$ continuously and SiC was gradually consumed, resulting in more gas in samples [7]. When samples were chilled-down in the furnace, the bubbles remained in samples and formed the pore bubble structure.

3.1.2 Bulk density and compressive strength

In Figure 4a., the bulk density and compressive strength decreased with the increase of sintering temperature. When the temperature raised, glass powder and perlite continued to melt, which provided sufficient reaction conditions for C0 samples. Thus the reaction proceed fully and the number of small pores increased gradually, resulting in the decreased of bulk density and compressive strength. Owing to the oxidation reaction of SiC, the compressive strength decreased significantly (4.68~2.31MPa) and
the bulk density decreased slowly (1.08~0.92 g/cm³) in the temperature range of 1400℃ to 1500℃. When SiC was oxidized into gas, the pore formation of C0 samples was obvious and the pore size was uniform. In Figure 4b., the bulk density decreased at a gentle rate and the compressive strength decreased significantly when samples were kept for 30min~120min. After 120 min, the compressive strength and bulk density suddenly changed because the mixture reacted sufficiently, resulting in the samples over burning. The existing small bubbles would merge into large bubbles, leading to the decrease of porosity and the increase of compressive strength. Therefore, the holding time of C0 samples should be less than 120min.

Figure 4. showed that sintering processes had an important influence on the bulk density and compressive strength of samples. By adjusting the sintering temperature and holding time, the chemical reaction between the matrix and SiC could be controlled, and the porosity and microstructure of samples could be regulated and controlled. When the sintering temperature was appropriately reduced, the gas would volatilize and leave melt holes, so as to kept uniform and dense closed pores in the samples. Finally the porous lightweight materials was obtained.

3.1.3 Porosity and heat conduction

![Graph](image)

Figure 5. Relationship between thermal conductivity and true porosity.
(a: C0 samples at different sintering temperatures b: C0 samples under different holding time).

Figure 5a. showed the pore size of C0 samples was larger with the increase of sintering temperature. With the increase of temperature, the pores produced by SiC reaction and C0 sample would gradually overburn. The secondary convergence and uneven distribution of pores made the density increase, so the thermal conductivity of samples increased, but the true porosity of samples decreased.

When the sintering temperature reached 1160℃, the thermal conductivity had the minimum value and the heat conduction effect was the best. The true porosity increased gradually with the increase of temperature. The true porosity of C0 samples changed significantly in the range of 1130℃ to 1140℃, the thermal conductivity and true porosity of C0 samples tended to be stable in the temperature range of 1150℃ to 1160℃. Figure 5b. verified that the thermal conductivity decreased with the appropriate extension of the holding time, C0 samples also had good thermal insulation performance. The compressive strength and the bulk density tended to decrease, however, the true porosity tended to increase. The thermal conductivity and true porosity would change suddenly when the holding time was 120min ~ 150min, so the holding time should not be too long.
3.1.4 Phase analysis

Figure 6. XRD spectra of C0 at different temperatures.

Figure 6. proved that there were hematite (Fe_2O_3), goethite [FeO (OH)], nepheline (NaAlSiO_4) and pyroxene (CaFeSi_2O_6) in C0 sample after fired. With the increase of temperature above 1130℃, goethite [FeO (OH)] disappeared due to the decomposition of hydroxyl groups. Fe_2O_3, Al_2O_3, SiO_2 and CaO in C0 would react with each other above 1100℃ to form quartz nepheline (NaAlSiO_4), pyroxene (CaFeSi_2O_6) and hibschite [Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}]. From XRD patterns, we could see that hematite (Fe_2O_3) and quartz (SiO_2) exist stably around 1130℃, and compared with the unsintered C0 mixture, the peak in the C0 sample after high temperature sintering started from scratch and remained stable.

3.1.5 Microstructure

Figure 7. SEM photos of C0 samples at different sintering temperatures.

(a: 1130 ℃  b: 1140 ℃  c: 1150 ℃  d: 1160 ℃).
The microstructure of samples was studied by SEM combined with pore size distribution histogram to discuss the effect of different sintering temperature on pore size distribution. The maximum pore size distribution (346.2μm~422μm) at 1130℃ was 7.5% and the average pore size was 180.72 μm (Figure 7a.). The maximum pore size distribution (544.1μm~601μm) at 1140℃ was 12.5% and the average pore size was 208.18μm (Figure 7b.). The maximum pore size distribution (814μm~900μm) at 1150℃ was 2.5% and the average pore size was 216.84μm (Figure 7c.). The maximum pore size distribution (714.2μm~881μm) at 1160℃ was 9% and the average pore size was 251.74μm (Figure 7d.).

As shown in Figure 7, that with the increase of sintering temperature, the maximum pore size and average pore size of samples showed an upward trend, which indicated that the sintering temperature played an important role in the pore size distribution of samples. The higher the sintering temperature was, the larger the pore size of samples was. The reaction of mixture was gradually sufficient with the increase of temperature, so as to further heating would make the small pores in samples converge into large bubbles, which made the maximum and average pore size of samples larger.

3.1.6 XEDS analysis

![XEDS spectrum of 1160℃ C0 sample.](image)

(Figure 8. XEDS spectrum of 1160℃ C0 sample. (G: point scan spectrum of C0 at 1160℃  E: point 1 spectrogram  F: point 2 spectrogram).
Figure 8. verified that the elements at point 1 were mainly silicon, aluminum, sodium, iron and a little titanium and the elements at point 2 were mainly silicon, aluminum, sodium, iron, and a small amount of potassium. Combined with the XRD spectrum of C0 at 1160℃, we could know that hematite existed stably, which corresponded to the XEDS spectrum of point 1 and point 2. The proportion of silicon atoms in point 2 was much larger than that in point 1. It was found that the punctate substance in Figure 8G. was iron and the glassy substance was silicate. The change of sintering temperature would not make the atoms in samples mutate, but the increase of temperature had a certain influence on the existence of silicon.

3.2 Iron oxide content

As a result of the iron oxide in red mud fluctuated greatly, the influence of its content were essential to furtherly studied on the bulk density, compressive strength, porosity and thermal properties of samples.

| Table 3. Comparison table of red mud and iron oxide content. |
|------------------------------------------------------------|
| Number | Iron oxide | Red mud |
|--------|------------|---------|
| C0     | 25.9       | 60      |
| C1     | 31.9       | 62      |
| C2     | 34.1       | 64      |
| C3     | 36.4       | 65      |

3.2.1 Bulk density and compressive strength

As shown in Figure 9., when iron oxide content reached 25.9%, the bulk density and compressive strength of samples had low values. With the higher iron oxide content, more and more pores could be seen but the pore size was generally small, which had not reached the ideal size. The mixture contained a large proportion of hematite that led to the raise of bulk density. Because of the crystal phase of iron oxide was different from that of pure glass, the increase of iron oxide content would lead to the raise of compressive strength. The pore size distribution of samples was uniform and dense, which indicated that iron oxide had a certain influence on the foaming temperature of samples and the existence of iron oxide could increase the foaming temperature of samples.
3.2.2 Porosity and heat conduction

Figure 10. indicated that with the increase of iron oxide content, the pore size of the sample became fine and uniform. With the increase of iron oxide content, there were small but not grown pores in the sample, which led to the decrease of true porosity. The decrease of porosity would inversely promote the increase of thermal conductivity and the iron oxide was a phase with high thermal conductivity, both of which increase the thermal conductivity. When the content of iron oxide reached 36.1%, the sample had high thermal conductivity and poor thermal insulation performance.

A theoretical model for the calculation of lightweight multiphase materials could be obtained from the empirical formula.

\[
\frac{\lambda_b}{\lambda_s} = \frac{p^{2/3} + \frac{\lambda_g}{\lambda_s}(1-p^{2/3})}{p^{2/3} + \frac{\lambda_g}{\lambda_s}(1-p^{2/3}) + p(1-p^{2/3})} \tag{3} \quad [10]
\]

\(\lambda_b\): the thermal conductivity of the light multiphase material \(w/(m\cdot K)\); \(\lambda_s\): the thermal conductivity of solid phase \(w/(m\cdot K)\); \(\lambda_g\): the thermal conductivity of the gas in the pore \(w/(m\cdot K)\); \(p\): the porosity of the lightweight multiphase material (%).

From the analysis of the above formula, it was found that the effect of parameters on the right side of formula (3) to \(\lambda_b\) was weaker than that of \(\lambda_s\). \(\lambda_s\) was the thermal conductivity of the solid stroma itself. With the increase of iron oxide content, the bulk density of the stroma increased and the thermal conductivity increased, too. Substituting the experimental data into (3), the change of porosity offset each other, \(\lambda_b\) increased. Referring to Figure 10, it could be seen that the thermal conductivity of porous materials increased with the increase of iron oxide content, which was consistent with formula (3), indicating that the thermal conductivity of porous materials was related to porosity and bulk density.
3.2.3 Phase analysis

Figure 11. XRD spectrum of C0, C1, C2, C3 (1150 °C, 120min).

Figure 11. explained that the forsterite (FeSiO₄), pyroxene (CaFeSi₂O₆), quartz (SiO₂) and hematite (Fe₂O₃) were the major phases in the samples. Most of the phases were stable. However, the peak of hematite (Fe₂O₃) was obviously stronger. Meanwhile, SiC reacted with iron oxide that enclosed in the high temperature melt to generate forsterite (FeSiO₄) and carbon dioxide.

3.2.4 Microstructure

Figure 12. SEM photos of samples with different formulations (1150°C, 120min) (a: C0 b: C1 c: C2 d: C3).
The effect of iron oxide content on the microstructure and pore size distribution of the samples were studied by SEM. Figure 12 showed that most of the pores of porous materials were closed and a few were open. Almost all obturator were independent. This structure could make the closed cell material absorb energy better for a good buffering performance and thereby make samples have higher strength.

According to Figure 12., the average pore size changed from 0.31mm to 0.19mm with the increase of iron oxide content. As a result, the pore size distribution of samples tended to decrease. The maximum and minimum values of samples pore size gradually decreased and samples pore size gradually became denser to achieve uniform. It was worth mentioning that the growth of samples bubbles was affected by the melting temperature. The increase of iron oxide content made samples pores increase rather than grow up, with the restriction from the iron oxide content and the melting temperature. With the increase of melting temperature, there were more melting environments that they were suitable for bubble growth, and small bubbles tend to become large bubbles. However, with the increase of iron oxide content, the melt viscosity of mixture became larger, which inhibited the growth of small bubbles, so the true porosity decreased.

4. Conclusion
The bulk density, compressive strength, thermal conductivity and true porosity of red mud based porous samples were studied by changing red mud content and firing process in this work.

- The sintering system had an important influence on the foaming mechanism of SiC. With the increase of sintering temperature and holding time, SiC reacted separately with oxygen and molten metal oxide to form gas. The gas accumulated in the melt to form bubbles. When the sample was cooled, the bubbles formed aggregation holes. With the further improvement of firing process, the reaction became more sufficient, with more bubbles formed. Consequently, the true porosity, compressive strength and thermal conductivity are increased.

- The content of iron oxide was closely related to the thermal conductivity of the sample. Iron oxide could increase the melting temperature and promote the complete reaction of the mixture, resulting in more bubbles. The higher the iron oxide content, the more the hematite content, resulting in the higher the compressive strength and the higher the thermal conductivity. That was because iron oxide increased the melt viscosity of the sample at high temperature, which inhibited the growth of small bubbles and reduced the true porosity. Due to iron oxide has high thermal conductivity, the above comprehensive effect increased the thermal conductivity of the sample and poor thermal insulation performance.

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References
[1] Change Liu, Nan Li, Yijiao Jiang, et al. (2006) Multipurpose Utilization of Slag from Aluminium Industry—Red mud. J. Yunnan Environmental Science, 03 : 39-41.
[2] Changjun Liu, Wencheng Li, Xiaoyan Zhou, et al. (2009) Study on basic characteristics of red mud by sintering process. J. Journal of Environmental Engineering, 04: 739-742.
[3] Tongyin Wang, Rui Li, Yihe Zhang, et al. (2020) Study on phase transformation in the preparation of red mud based porous thermal insulation materials with low thermal conductivity. J. Comprehensive utilization of resources in China, 11: 23-29.
[4] Hongshan Wei, Xiaoe Ma, Xuemao Guan, et al. (2017) Study on lightweight thermal insulation ceramic material with large amount of Bayer red mud. J. Light metal, 04: 16-19.
[5] Qiangtao Wang,Sen Li,Fengzhi Li,et al. (2017) Effect of red mud content on properties of thermal insulation decorative building ceramics. J. Non-Metallic Minerals, 05: 41-44.
[6] Xuewei Luo, Yiren Chen, Huang Zhao, et al. (2016) Research progress in preparation of foamed ceramic insulation board from aluminum silicon solid waste. In: Proceedings of the 7th
technical seminar on comprehensive utilization of tailings and metallurgical slag and Zhaoyuan circular economy project investment docking meeting. Zhaoyuan. pp. 8.

[7] Huining Huang, Shanjun Ke, Guotao Zhang, et al. (2021) Application and present situation of polishing waste residue in ceramic brick. J. Foshan Ceramics, 07: 1-9.

[8] Lin Li et al. (2020) The influence of temperature and SiC content on the recycling of iron ore tailings for the preparation of value-added foam ceramics. J. Journal of Material Cycles and Waste Management, : 1-11.

[9] Aiqin Wang, Min Li, Jingpei Xie, et al. (2015) Interfacial chemical reaction analysis of pretreated SiCp and SiCp / A390 Composites. Collected works of 2015 China Foundry week. Changsha. pp. 7.

[10] Qunhu Xue, Weizhong Xu. (2015) Refractory. Metallurgical industry press, Beijing.