Preparation and Characteristics of Porous Ceramics by a foaming Technology at Low Temperature

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Abstract. Recycling and converting coal gangue and red mud into porous ceramics with good performance is a feasible disposal route. In this present work, porous foam ceramics was prepared using coal gangue and red mud as main raw materials at low sintering temperature. The amount of coal gangue and red mud were up to 70 wt%. To regulate the forming and sintering performance of the product, quartz sands and clay material were added to the formula. The green body was formed by a foaming technology using aluminum powders as foaming agents at room temperature. After foamed, the specimens were dried at 60-80 °C, and then calcined at 1060 °C. Effects of concentration of NaOH and amount of aluminum powders on the phase, mechanical properties and microstructure were investigated here. Such study is expected to provide a new utilization route of the coal gangue and red mud, and brings both intensive environmental and economic benefits.

1. Introduction

With the rapid development of industrial technology, all kinds of industrial solid wastes also increase year by year. In China, red mud and coal gangue are the prominent solid waste produced by the aluminum processing and coal mining and processing. Simply stockpile and stacking treatment continue to still be used now, which not only occupy too much land, also give rise to serious environmental problems and huge waste of resources\cite{1}, \cite{2}. Therefore, it is vital to develop a comprehensive utilization technology that consumes red mud and coal gangue or converts them into a secondary resource. Up to now, scientists have carried out research projects to explore disposal and utilization routes of these wastes. According to their unique physical and chemical properties, it has been found that they could be utilized to produce environmental protection product for adsorption to purify water\cite{3}, light weight aggregate concrete and cementitious materials\cite{4-6}, traditional clay brick and ceramic products\cite{4, 7-8}. Nevertheless, their use dosage is limited in a low percentage, especially for red mud, and their comprehensive utilization rate in China was less than 4\% for red mud and 60\% for coal gangue, respectively \cite{1,9}.

Porous ceramic materials have several unique properties such as low density, low thermal conductivity, high surface area, high permeability, etc., and widely used as filters, catalyst supports,
refractory linings for furnaces, or sound proof materials. There are various processing methods for fabricating the porous ceramics, such as: burn-out of organic pore-formers, replication of polymeric sponges, foaming of suspensions, sintering of spherical particles and freeze casting [10]. These methods allow obtaining materials of different porosity, poring size and poring geometry. Unfortunately, although considerable attention is paid on obtaining a porous ceramic materials, there are few reports about the preparation of porous ceramic products mainly using coal gangue and red mud by a foaming techniques at a low sintering temperature so far. Therefore, in the present work, effects of different pore creators and pore stabilizers on the mechanical property, porosity and pore microstructure of the foam ceramics would be discussed.

2. Experimental

2.1. Raw Materials
The red mud and coal gangue were supplied by industrial enterprises in Shanxi, CHINA. The chemical composition of the major raw materials used here is shown in Table 1. Aluminum powders and NaOH solution were added as the foaming agents.

2.2. Preparation of porous materials
All the raw materials were ball-milled in a wet condition for 15 min, their mass percentage for each ingredient was shown in Table 2. After drying the slurry in an electric oven at 110 °C, the mixed materials was re-crushed in a dry condition and sieved pass 150 mesh. The mixture was then wet-mixed with aluminum powders and NaOH solution in different proportions for 3 min.

Rectangular silicone molds were employed for molding the green specimens, the batch was dried at 110°C for 1 h after foaming at 40 °C for 2 h. Finally, the dried specimens were calcined at 1060 °C at a heating rate of 6 °C/min and naturally cooling.

2.3. Characterization of porous ceramic samples
The chemical composition of raw materials was determined by X-ray fluorescence analysis. The bulk density and apparent porosity of products were measured and calculated by the Archimedes method. The flexural strength of samples was directly measured with regular dimension. Appreciation of crystalline phases of the products was done on X-ray diffraction. The microstructure was analyzed through observing the cross sections of fractured samples via optical microscope.

Table 1. Chemical compositions of the raw material

| Raw Materials    | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | TiO₂ | P₂O₅ | ZrO₂ |
|------------------|------|-------|-------|-----|-----|-----|------|------|------|------|
| Red mud          | 27.22| 25.76 | 5.72  | 21.78| 0.90| 1.32| 11.81| 4.85 | 0.42 | 0.16 |
| Coal gangue      | 57.59| 25.46 | 8.87  | 4.30 | 0.70| 1.30| 0.36 | 1.25 | 0.16 |
| Clay mineral     | 62.50| 20.64 | 5.72  | 0.45 | 0.69| 3.05| 0.74 | 0.15 |
| Quartz           | 98.40| 0.55  | 0.10  | 0.25 | 0.35|

3. Results and discussion
Porosity and flexural strength of the product and forming performance of the green body were found to depend on the water addition amount, concentration and volume of the NaOH solution, as well as the amount of the aluminum powders. In the present paper, a new moulding process was conducted by casting and foaming. To obtain a suitable slurry with good flow-ability and foaming behaviour, addition amount of water was ranged from 45–60 wt% according to the ingredient formula of the specimens. It was found that low water addition greatly increased the viscosity of the slurry, greatly impairing the foam formation and giving rise to a dense green body. With the increase of water addition, the viscosity became low, favouring the foam formation and the obtainment of suitable pore
size. The appropriate water addition proportion should be controlled to 50–52 wt% for moulding and foaming of the green body.

**Table 2. Specimen composition**

| Sample | Red mud (wt%) | Clay mineral (wt%) | Coal gangue (wt%) | Quartz (wt%) | NaOH (mol/L) | Al powders (wt%) |
|--------|---------------|-------------------|------------------|--------------|--------------|-----------------|
| A1     |               |                   |                  |              | 0.03         |                 |
| A2     | 20-25         | 25-30             | 45-50            | 5-10         | 0.75         | 0.04            |
| A3     |               |                   |                  |              | 0.05         |                 |
| B1     | 20-25         | 25-30             | 45-50            | 5-10         | 0.50         | 0.05            |
| B2     |               |                   |                  |              | 0.03         |                 |
| B3     |               |                   |                  |              | 0.05         |                 |
| C1     | 20-25         | 25-30             | 45-50            | 5-10         | 0.25         | 0.04            |
| C2     |               |                   |                  |              | 0.05         |                 |
| C3     |               |                   |                  |              | 0.03         |                 |
| D1     | 20-25         | 25-30             | 45-50            | 5-10         | 0.10         | 0.04            |
| D2     |               |                   |                  |              | 0.05         |                 |
| D3     |               |                   |                  |              | 0.03         |                 |

Figure 1 shows the flexural strength and porosity of the ceramic specimens prepared with 68% red mud and coal gangue against the different sodium hydroxide solution concentration. With the increase of NaOH concentration, the flexural strength of porous ceramics increased firstly and then decreased, reaching a maximum value at 0.5mol/L NaOH. Under low concentration conditions, such as 0.1mol/L NaOH, since the amount of H₂ produced by the reaction of aluminum with water increased with its amount in the slurry, the internal pore size and pore content in the materials also increased, giving rise to a decrease in their flexural strength with the increase of the amount of aluminum powders. When the NaOH concentration was more than 0.5 mol/L, the reaction rate of aluminum with water was greatly accelerated, yielding more H₂ in a short time, which would lead to bubble coalescence easily.

![Figure 1](image1.png)

(a) Change in flexural strength  
(b) Change in porosity

**Figure 1.** Changes of flexural strength and porosity of specimens against NaOH solution concentration

In such a condition, further increasing the amount of aluminum powders would impair the foam formation. Thus, the foaming effect of aluminum powders was related to both the concentration of NaOH and the content of aluminum powders.
As shown in Figure 1b, the porosity of the samples increased with the increase of NaOH concentration, but the change was slightly when the NaOH concentration was in 0.1-0.5 mol/L, which was speculated to be related to the porosity and pore distribution of the materials. When the NaOH concentration was less than 0.25 mol/L, the porosity increased with the amount of aluminum powders. However, when the NaOH concentration was > 0.5 mol/L, the porosity of the materials decreased due to the increase in the probability of occurrence of a large number of pores and bubbles.

Figure 2 shows the XRD pattern of specimens calcined at 1060°C using 50% coal gangue and 20% red mud, which was formed using 0.03 wt% Aluminum powders and 0.5 mol/L NaOH. Its major crystalline phases were mainly composed of quartz and Ca(Al₂Si₂O₈) or Na(AlSi₃O₈). High baseline also indicated the existence of the glass phase in the products. No obvious change in the phase composition was found for the samples by various amounts of Aluminum powders.

![XRD pattern of porous ceramic prepared with 0.03 wt% aluminum powders](image)

**Figure 2.** XRD patterns of porous ceramic prepared with 0.03 wt% aluminum powders

Figure 3 shows the surface morphology of the specimens prepared with 0.25 mol/L, 0.5 mol/L, 0.75 mol/L NaOH and 0.03 wt% aluminum powders. All the samples possessed high porosity. A large number of pores ranged from 0.5 to 2 mm could be seen on the fractured surface. With the increase of NaOH concentration, the pore size and porosity of the foam ceramics gradually increased, and their pore distribution was also improved gradually. The foaming performance of the materials was closely related with the content of aluminum powders and the reaction condition with water. With the increase of NaOH concentration, the more bubbles were generated by the reaction of Al powders and NaOH solution, the more pores were formed in the corresponding slurry, and the more pores are formed after forming, drying and sintering.

![Surface morphology of specimens with 0.03wt% aluminum powders and different NaOH concentration](image)

**Figure 3.** Surface morphology of specimens with 0.03wt% aluminum powders and different NaOH concentration 1000

4. **Summary**
Red mud and coal gangue was utilized to prepare the foam ceramic materials; its utilization amount could be up to 70 wt% when using aluminum powders as the foaming agents. The foaming
performance of the materials was closely related with the content of aluminum powders and the reaction condition with water solution. Utilization of red mud and coal gangue for preparing porous ceramics with good performances was expected to provide a feasible disposal of landfill and soil fail problems caused by deserted slag.

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