Research Article

Sulfur Fixation by Chemically Modified Red Mud Samples Containing Inorganic Additives: A Parametric Study

Yang Liu, Yang Li, Feng-shan Zhou, Ying-mo Hu, and Yi-he Zhang

Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences (Beijing), Beijing 100083, China

Correspondence should be addressed to Feng-shan Zhou; zhoufs@cugb.edu.cn

Received 23 January 2016; Revised 8 June 2016; Accepted 17 July 2016

Academic Editor: Santiago Garcia-Granda

Copyright © 2016 Yang Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Sulfur retention ability of Bayer red mud from alumina plant was investigated. Bayer red mud modified by fusel salt and waste mother liquor of sodium ferrocyanide as the main sulfur fixation agent and the calcium based natural mineral materials as servicing additives; the experimental results showed the following: (1) Through 10 wt% waste mother liquor of sodium ferrocyanide modifying Bayer red mud, sulfur fixation rate can increase by 13 wt%. (2) Magnesium oxide can obviously improve the sulfur fixation performance of Bayer red mud and up to a maximum sulfur fixation rate of 47 wt% at adding 1 wt% magnesium oxide. (3) Dolomite enhanced the sulfur fixation performances with the sulfur fixation rate of 68 wt% in optimized condition. (4) Vermiculite dust reduced sulfur dioxide during the fixed-sulfur process of modified Bayer red mud, and the desulphurization ration could reach up to a maximum 76 wt% at 950°C. (5) An advanced three-components sulfur fixation agent was investigated, in which the optimized mass ratio of modified Bayer red mud, dolomite, and vermiculite dust was 70 : 28 : 2 in order, and its sulfur fixation efficiency has reached to a maximum 87 wt% under its 20 wt% dosage in the coal.

1. Introduction

Since the 1980s, with the rapid development of China’s economy, the annual consumption of coal has been increasing by a large margin and China has become the largest producer and consumer of coal [1]. The main pollution of China is derived from emissions of SO₂ and dust caused by coal combustion. Therefore, the control of SO₂ emitted from industrial coal-fired boilers has great significance for air pollution control in our country [2]. Desulphurization technology is the main method to reduce SO₂ pollution [3]. At present, the commonly used desulphurization technology includes desulphurization before combustion, sulfur fixation during combustion, and flue gas desulphurization [4]. Developing a new type of sulfur fixing agents has become the most valuable industrial desulphurization technical way in coal combustion process [5]. At present, the mainly used sulfur-fixing agents at home and abroad include calcium-based, magnesium-based, sodium-based, and potassium-based sulfur-fixing agents [6–9]. Traditional calcium-based sulfur-fixing agent (limestone, dolomite, etc.) generally showed the disadvantages of low calcium utilization rate and low sulfur fixation rate at high temperature [10].

In recent years, many domestic and foreign researchers found that the sulfur-fixing efficiency of coal combustion could be improved by modifying the fixing agents using sodium chloride [11], ethanol, and acetic acid [12] or adding Fe₂O₃, SiO₂, Al₂O₃, and Na₂CO₃ [13–18] to the sulfur-fixing agents.

In addition to the researches of sulfur-fixing additive, some industrial solid waste is also used as desulphurization agents such as Carbide slag, black liquor of papermaking, and red mud [19–26]. Bayer red mud is an industrial solid waste with high alkalinity and environmental impact, which is discharged during the process of Al₂O₃ extraction from bauxite in alumina plant. Disposal of Bayer red mud occupies large areas of productive land, and it is harmful to the environment due to its high alkalinity, heavy metals, and sometimes radioactivity [27–29]. Red mud is mainly composed of fine particles including Al₂O₃, Fe₂O₃, CaO, MgO, and Na₂O [19, 20]. Owing to its high alkalinity and chemical properties, Bayer red mud could be used as a kind...
of sulfur-fixing agent. This not only opens up a new way for the utilization of red mud but also finds a cheap and efficient sulfur-fixing agent for the coal industry.

In recent years, many domestic and foreign scholars focused their research on red mud slurry for flue gas desulfurization [21, 22]. But the red mud slurry is easy to harden and not conducive for long time use [23]. By adding natural minerals to Bayer red mud, a high performance synergistic sulfur-fixing agent was developed for sulfur fixation during coal combustion in the present work. According to the sulfur-fixing product of sulfur-fixing agent, we will continue to study the preparation of oilfield waste drilling fluid treatment agent using the sulfur-fixing product, which will truly achieve high value-added and clean utilization of red mud.

2. Materials and Methods

2.1. Materials

Raw Coal. Raw coal came from Zouping Weimian Corporation (Shandong, China). The total sulfur content in the coal sample was determined by Eschka method [30]. 0.2 g coal (200 mesh) was mixed with Eschka reagent and burned. The sulfur in the coal reacted with Eschka reagent to produce sulfate. Then, sulfate ions (SO$_4^{2-}$) reacted with barium ions (Ba$^{2+}$) to produce barium sulfate (BaSO$_4$). The total sulfur content was calculated according to the produced weight of BaSO$_4$. Experimental results showed that the total sulfur content of the raw coal was 1.685 wt%. According to the classification standard of sulfur coal [31], the raw coal belongs to the middle sulfur coal.

Bayer Red Mud. The red mud in the present work in the form of dried clay was obtained from Zhengzhou Great Wall Alumina Corporation (Henan Province, China). Table 1 shows the component contents of the red mud. The XRD pattern and its particle size distribution of the red mud sample are shown in Figures 1 and 2. The particle size of the red mud was in the range of 0.1–500 mm (generally finer than 200 mesh after drying and grinding). The mineral compositions of the Bayer red mud were very complicated [32], but the content of Al$_2$O$_3$ and SiO$_2$ was relatively high with 24.35 wt% and 18.12 wt%.

Modification Agents. Modification agents were the byproduct of yellow blood sodium (sodium ferrocyanide) solution from Hebei Chengxin Co., Ltd. (Hebei, China), and fusel alcohol salts from Changchun Dacheng Industry Company (Jilin, China). The chemical composition was shown in Tables 2 and 3.

Sulfur Fixation Additives. Magnesium oxide (MgO, industrial grade, purity more than 95 wt%) was obtained from Beijing Chemical Plant. The natural mineral materials brucite and dolomite were obtained from Dandong Yilong Gaoke New Material Co., Ltd. (Liaoning, China); both of their particle sizes were in the range of 800–1000 mesh.

2 Advances in Materials Science and Engineering

<table>
<thead>
<tr>
<th>Components</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>MgO</th>
<th>Water</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/wt%</td>
<td>24.35</td>
<td>19.96</td>
<td>18.12</td>
<td>7.79</td>
<td>5.54</td>
<td>1.47</td>
<td>0.87</td>
<td>14.25</td>
</tr>
</tbody>
</table>

Table 1: Chemical composition of Bayer red mud in the present work.
Table 2: Chemical composition of waste mother liquor of sodium ferrocyanide.

<table>
<thead>
<tr>
<th>Components</th>
<th>Na$_2$Fe(CN)$_6$</th>
<th>HCOONa</th>
<th>Na$_2$CO$_3$</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/wt%</td>
<td>5.29</td>
<td>39.83</td>
<td>5.27</td>
<td>49.31</td>
</tr>
</tbody>
</table>

2.2. Laboratory Instruments. The pH of red mud suspension in the reaction process was measured by pH500 meter. The chemical analytical methods of Al$_2$O$_3$, CaO, and MgO were Karl Fischer titration, SiO$_2$ by gravimetry, and Fe$_2$O$_3$ by colorimetry and K$_2$O/Na$_2$O was determined by FP-640 Flame Photometer. The XRD patterns of the samples were determined by X-ray diffractometer with a Cu Ka (0.15418 nm) radiation source in a 2θ range of 10°–70° at a scanning rate of 2° min$^{-1}$. The morphologies of red mud were analyzed by Hitachi S-4800 high resolution ice emission scanning electron microscopy (SEM) [33].

Both of the SK-G10123K Tube furnace and the SK-G18123 Muffle furnace were purchased from Zhonghuan Experiment Electric Furnace Co., Ltd. (Tianjin, China). Heating rate of the SK-G10123K Tube furnace was 5°C/min at below 500°C, 10°C/min at 500–800°C, 5°C/min at 800–1000°C, and less than 2°C/min at 1000–1200°C. The length of its heating zone was 420 mm, and its constant temperature zone was 200 mm. Muffle furnace SK-G18123 Model with resistance wire heating was used; its heating process was 100°C to the maximum 1200°C in 40 min.

2.3. Experimental Methods

2.3.1. Modification Experiment of Bayer Red Mud. The Bayer red mud was immersed in modification agents with certain concentration for 24 h. Then, it was taken out and dried in an oven at constant temperature of 80°C for 12 h. Finally, it was taken out from the oven, milled, and screened as a reserve. Particle size distribution of original and modified Bayer red mud is shown in Figure 2.

2.3.2. Sulfur Fixation Experiment. Sulfur fixation for combustion coal was carried out in the SK-G10123K Tube furnace. The furnace was heated to 950°C according to its heating rate procedure firstly; then the specified amount of coal sample mixed sulfur fixation agents beforehand was loaded in a combustion boat, the coal sample was pushed slowly to the furnace inside, and finally air was pumped into the furnace to make a full combustion of the coal sample.

2.3.3. The Calculation of Sulfur Fixation Rate and the Utilization Rate of Calcium. The sulfur content was determined by using chemical analysis method. The sulfur fixation efficiency $\eta$ (see (1)) and the utilization rate of calcium $\eta_{Ca}$ (see (2)) [26, 34] were determined by testing the total sulfur content in coal ash and the coal sample:

$$\eta = \frac{m_2 \times S_{ad}}{m_1 \times S_{fad}} \times 100\%,$$  

$$\eta_{Ca} = \frac{S_{ad} \times m_2 \times 56}{32 \times M_{CaO}\times W_{CaO}} \times 100\%,$$

where $\eta$ is sulfur fixation efficiency; $m_1$ is experimental coal sample mass, g; $m_2$ is total mass of ash after combustion, g; $S_{ad}$ is the sulfur content of ash, wt%; $S_{fad}$ is total sulfur content of experimental coal sample, wt%. Consider

3. Results and Discussion

3.1. Influence of Ca/S Mole Ratio on the Sulfur Fixation Effect. The Ca/S mole ratio is one of the main factors that affect the sulfur fixation effect. Using Bayer red mud as the sulfur fixation agent, the influence of Ca/S mole ratio on the sulfur fixation efficiency was studied. The results were shown in Figure 3.

Figure 3 indicated that the sulfur fixation rate increased with the increase of the Ca/S mole ratio when Bayer red mud was used as sulfur fixation agent. However, the increase of the Ca/S mole ratio would greatly increase the amount of sulfur fixation agent and reduce the heating rate of the coal. So, the doping content of Bayer red mud in the following experiment was optimized to be 10 wt% (the mole ratio of Ca/S was 0.7).

3.2. The Influence of Modification on the Sulfur Fixation Effect

3.2.1. The Influence of Modification on the Sulfur Fixation Efficiency. Experimental results indicated that the maximum sulfur fixation efficiency of original Bayer red mud was only 42.83 wt% when the mass dosing of red mud as sulfur fixation agent was 20 wt% coal sample. Modification activation method was used to improve the sulfur fixation efficiency of red mud. Fusel salt and waste mother liquor of sodium ferrocyanide were used as modification agents. The influence
Table 3: Chemical composition of the fusel salt.

<table>
<thead>
<tr>
<th>Components</th>
<th>Ethylene glycol, propylene glycol, butyl glycol, glycerin, and so forth</th>
<th>Salt mix (sodium formate, sodium acetate and sodium lactate, etc.)</th>
<th>Polyether polyols (low polymerization degree)</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/wt%</td>
<td>35–45</td>
<td>20–30</td>
<td>25–35</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Table 4: Effect of the fusel salt on sulfur fixation of modified Bayer red mud.

<table>
<thead>
<tr>
<th>Amount/wt%</th>
<th>0</th>
<th>10</th>
<th>30</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content in the residue/wt%</td>
<td>0.667</td>
<td>0.877</td>
<td>1.171</td>
<td>1.684</td>
</tr>
<tr>
<td>Utilization rate of Ca/wt%</td>
<td>10.20</td>
<td>16.20</td>
<td>21.95</td>
<td>31.61</td>
</tr>
<tr>
<td>Sulfur fixation rate/wt%</td>
<td>8.333</td>
<td>12.06</td>
<td>17.87</td>
<td>23.54</td>
</tr>
</tbody>
</table>

Table 5: Effect of the waste mother liquor of sodium ferrocyanide on sulfur fixation of modified Bayer red mud.

<table>
<thead>
<tr>
<th>Amount/wt%</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content in the residue/wt%</td>
<td>0.667</td>
<td>1.876</td>
<td>2.63</td>
<td>2.224</td>
</tr>
<tr>
<td>Utilization rate of Ca/wt%</td>
<td>10.20</td>
<td>40.10</td>
<td>26.43</td>
<td>23.64</td>
</tr>
<tr>
<td>Sulfur fixation rate/wt%</td>
<td>8.333</td>
<td>29.85</td>
<td>20.58</td>
<td>18.48</td>
</tr>
</tbody>
</table>

Table 6: Specific surface area (SSA) of modified Bayer red mud before and after sulfur fixation reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area with BET method (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Bayer red mud</td>
<td>14.100</td>
</tr>
<tr>
<td>Bayer red mud modified by 50 wt% fusel solution</td>
<td>99.086</td>
</tr>
<tr>
<td>Bayer red mud modified by 10 wt% sodium ferrocyanide solution</td>
<td>142.300</td>
</tr>
<tr>
<td>Sulfur fixation ashes formed at 950°C after the sulfur fixation reaction of three-componentsulfur fixation agent SFG-2</td>
<td>176.179</td>
</tr>
</tbody>
</table>

of different amount wt% of fusel salt and waste mother liquor of sodium ferrocyanide on the sulfur fixation efficiency of Bayer red mud was studied.

The results of Tables 4 and 5 and Figure 4 indicated that the sulfur fixation efficiency could increase by 7 percentage points after the Bayer red mud was modified by 50 wt% fusel solution. Meanwhile, the utilization efficiency also increased from 22.02 wt% to 31.61 wt%. But the red mud after fusel modification was not easy to be dried and crushed and the mixing was not uniform. For the 10 wt% sodium ferrocyanide modified Bayer red mud, the sulfur fixation efficiency could increase by 13 percentage points and the utilization efficiency increased to 40.10 wt%.

3.2.2. The Influence of Modification on the Surface Morphology of Bayer Red Mud. The results of Scanning Electronic Micrography (SEM) indicated that the morphology of the Bayer red mud modified by fusel salt and sodium ferrocyanide changed after calcination at 950°C (Figure 5). Non-significant structural change was observed in the three samples in Figure 5, but the sodium ferrocyanide modified sample showed a relatively more change in the formation of porous structure. Agglomeration was still noticeable in unmodified and modified red mud. The particles of unmodified Bayer red mud agglomerated more seriously, which was not conducive to the diffusion of SO₂ and the sulfur fixation reaction. In contrast, the secondary pore structure in the modified sample was beneficial to the diffusion of the gases and promoted the sulfur fixation reaction. It was possible that the specific surface area (SSA) and porosity increased the fixation degree. Figure 6 shows the secondary porous structure after sulfur fixation reaction of modified red mud; the SSA has indeed increased (Table 6). As predecessors had proposed that the influence of pore structure characteristics on their sulfur fixation performance was very important, little pores made a significant contribution to alkaline substance utilization in the initial stage of reaction and at lower temperature, while bigger pores took effect in the later stage and at higher temperature. The more the pore in range of effective aperture, the better the sulfur fixation performance [35].

3.3. The Influence of Additives on the Sulfur Fixation Efficiency. Because single modified Bayer red mud showed lower sulfur fixation efficiency, it was necessary to add some additives to improve sulfur fixation efficiency. In this paper, the effects of additives of magnesium containing were mainly studied.

3.3.1. The Influence of MgO on the Sulfur Fixation Efficiency. MgO additives with doping content of 1 wt%, 2 wt%, and 3 wt% were added together with Bayer red mud to the coal samples. Experimental results of Figures 7 and 8 indicated that MgO significantly improved the sulfur fixation efficiency of the combustion coal. With the increase of MgO doping content, the sulfur fixation efficiency showed a decreasing trend after the first increase. The sulfur fixation efficiency was optimized to be 46.56 wt% when the doping content of MgO was 1 wt%.
During the sulfur fixation process, SO₂ transformed into sulfate by reacting with MgO. Meanwhile, MgO showed catalytic effects on sulfur fixation reaction for combustion of coal [36]. So the addition of MgO increased the sulfur fixation efficiency and improved the utilization rate of calcium (the highest utilization rate could reach 56.35 wt%).

3.3.2. The Influence of Natural Mineral Materials Additives on the Sulfur Fixation Efficiency. Both of dolomite and brucite with doping content of 1 wt%, 2 wt%, 3 wt%, and 4 wt% were added together with Bayer red mud to the coal samples. The influence of dolomite and brucite on the sulfur fixation efficiency of the combustion coal was studied, respectively. The sulfur fixation efficiency increased with the addition of the two natural mineral materials (Figure 9). As an effective sulfur fixation mineral material, dolomite was better than brucite. The sulfur fixation efficiency was optimized to be 67.70 wt% when the doping content of dolomite was 4 wt%. Meanwhile, the paper researched the effect of the mass ratio of brucite and dolomite (4:0, 3:1, 2:2, 1:3, and 0:4) on the sulfur fixation efficiency. According to Figure 10, the results showed that the efficiency of sulfur fixation was different under the same temperature but different dolomite/brucite...
ratio; with the dolomite increasing or brucite decreasing, the sulfur fixation increased, and the sulfur fixation efficiency was maximum 67.70 wt%; with the only doping content of dolomite was 4 wt%. According to above results, the paper selected dolomite as the additives of sulfur fixation agents and developed a new kind of sulfur-fixed agent named SFG-1 which is composed of modified Bayer red mud and dolomite with the mass ratio of 10:4 in order. At 950°C, CaO and MgO derived from the decomposition of dolomite and brucite could react with SO$_2$, showed a certain catalytic effect on sulfur fixation reaction, and improved the sulfur fixation efficiency. Besides, adding dolomite could improve pore structure of the red mud after high temperature calcination, accelerate the forming of high temperature stability of sulfide minerals, and restrain the decomposing of CaSO$_4$ [19], which made the sulfur fixation efficiency improved. And the existence of dolomite can improve the pore structure of red mud in high temperature, which also enhanced the own desulfurization efficiency of Bayer red mud.

3.4. The Influence of Promoter on the Sulfur Fixation Efficiency. In order to further improve the sulfur fixation effect of combustion, the promoter added again by experimental design. Although the layered structure and dilatability of vermiculite promoted the inner oxidation extent of the coal combustion and enhanced the fixed-sulfur efficiency [37], vermiculite was difficult to crush because of its good toughness, so as to increase the cost of crushing. However, the dust from vermiculite industry was mainly composed of fine particles (160–200 mesh) and had high specific surface area. Using the vermiculite dust replacing normal industrial vermiculite as coal-burning sulfur-fixed promoter, the effect of different doping content of vermiculite dust (0.1 wt%, 0.2 wt%, 0.3 wt%, and 0.4 wt%) on fixed-sulfur efficiency was researched.

According to the experimental results (Figure 11), vermiculite dust could promote the fixed-sulfur efficiency. Experimental results showed that vermiculite dust played an important role in reducing SO$_2$ during the fixed-sulfur process of modified Bayer red mud or SFG-1, and the desulphurization ration could reach up to maximum 76 wt% at 950°C. The main reasons were that further inflating of vermiculite dust at 950°C could make the inner looser and promote the inner oxidation extent of the coal combustion,
3.5. \textit{The Influence of SFG-2 on the Sulfur Fixation Efficiency.} The influence of SFG-2 content ranging in the coal from 10 wt\% up to 25 wt\% on the sulfur fixation efficiency was studied. Experimental results (Figure 12) showed that SFG-2 achieved desulphurization ration maximum 87 wt\% when the doping content of SFG-2 in the coal was up to 20 wt\% (i.e., Ca/S mole ratio was 1.3), and it may be inferred that the tricomponent composite SFG-2 was indeed an advanced desulphurization material.

3.6. \textit{XRD of Desulphurization Produced Ashes.} The structural characteristic of desulphurization produced ashes was investigated by X-ray diffraction (XRD), and the analysis results of the produced ashes used SFG-2 as sulfur fixation agent at 950\(^\circ\)C were shown in Figure 13. The diffraction structural peaks of CaSO\(_4\), Fe\(_2\)O\(_3\), Ca\(_2\)Al\(_2\)SiO\(_7\), and (Na,Ca)Al(Si,Al)\(_3\)O\(_8\) could be clearly found, especially CaSO\(_4\), which showed that CaSO\(_4\) was the main component of sulfur fixation produced ashes at 950\(^\circ\)C and the content is more. Besides, the existence of Ca\(_2\)Al\(_2\)SiO\(_7\) and (Na,Ca)Al(Si,Al)\(_3\)O\(_8\) also improved the sulfur fixation efficiency [32].

4. Conclusion

(1) The sulfur fixation rate of Bayer red mud could be improved by using fusel salt and waste mother liquor of sodium ferrocyanide as the modifying agents. When 50 wt\% fusel salt solution was used as
modifying agent, the sulfur fixation rate increased by 7 wt% and the utilization rate of calcium increased from 22.02 wt% to 31.61 wt%. When modified by waste mother liquor of sodium ferrocyanide with the concentration of 10 wt%, sulfur fixation rate could increase by 13 wt%, the highest of which could reach 29.85 wt% and the utilization rate of calcium reached 40.10 wt%.

(2) Magnesium oxide (MgO) could obviously improve the sulfur fixation performance of Bayer red mud and up to a maximum sulfur fixation rate of 46.56 wt% with the 1 wt% MgO adding.

(3) The sulfur fixation efficiency increased with the addition of the two natural mineral materials. Dolomite showed better effect than brucite. And the efficiency of sulfur fixation was different at 950°C with different dolomite/brucite ratio. With the dolomite increasing and brucite decreasing, the sulfur fixation increased. The sulfur fixation efficiency was 67.70 wt% when the sulfur fixation agent consisted of 10 wt% Bayer red mud and 4 wt% dolomite.

(4) Vermiculite dust could promote the fixed-sulfur efficiency. The main reasons were that further inflating of vermiculite dust at 950°C could make the inner looser and promote the inner oxidation extent of the coal combustion, which was advantageous to forming CaSO₄ and restraining the decomposing of CaSO₄.

(5) A new kind of tricomponent complex sulfur fixation agent SFG-2 was made successfully, in which modified Bayer red mud was the main desulphurization composition, dolomite served as additives, vermiculite dust played the inflation role, and the optimized mass ratio in order was 70 : 28 : 2. The SFG-2 achieved desulphurization ration maximum 87 wt% when the doping content of SFG-2 in the coal was 20 wt% (i.e., Ca/S mole ratio was 1.3), which indeed proved the advanced desulphurization characteristics of SFG-2.

Competing Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors’ Contributions
Yang Liu and Yang Li contributed equally to this work.

Acknowledgments
This research was supported by the National High Technology Research and Development Program of China (863 Program 2012AA06A109).

References


