The fractal properties of calcination of limestone and its sulfidation with H$_2$S

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Abstract—Fractal geometry was used to describe the calcination of limestones and the sulfur-removal process performed in TGA instrument, and the fractal dimension was calculated through the nitrogen adsorption. The effect of calcination of limestones on the porous structure and fractal dimension of calcined limestones was investigated, and the highest value of fractal dimension 2.72 can be obtained at 850℃. The fractal dimension will reduce with the increase of limestones particle size. The fractal dimension of calcined limestones has a significant influence on the sulfur-removal reactivity. It can be stated that the highest reaction reactivity can be obtained when the calcined limestone has a moderate fractal dimension of 2.70.

Keywords- limestone; calcination; sulfur-removal; fractal dimension

I. INTRODUCTION

Advanced power generation systems, such as the second generation pressurized fluidized bed combustion- combined cycle (2G PFBC-CC) and the integrated gasification combined cycle (IGCC), are expected to realize much higher efficiency if sulfur compounds can be removed under high temperature. During the 2G PFBC-CC, coal is partially gasified in a carbonizer to produce pressurized gases with low heat value; the gases are then introduced into the combustion chamber to raise the temperature of the gases into the turbine. During gasification, sulfur in the fuel is released and must be removed. The desulfurization under high temperature has higher cycle efficiency and is a research focus. Among the numerous desulfurization sorbents, the calcium sorbents with low price have higher reaction temperature compared with the metal sorbents, so the calcium sorbents are often recommended, and the most commonly used is limestone.

As we all know, the pore structure play a significant role in the sulfidation of limestone with H$_2$S, how to measure the complex pore structure of the sorbents and to understand its effect on the sulfidation is a key question.

Since the fractal theory is proposed by Mandelbrot [1], it is a powerful tool to study the rough or fragmented geometric shape and is widely used in many fields. Fractal dimension is a statistical quantity that gives an indication of how completely a fractal appears to fill space, which is the most important scale parameter for a fractal. The value of fractal dimension can vary from 2 to 3, the larger fractal dimension, the more complex the fractal surface is. It was reported that the fractal theory had been used to the SO$_2$ removal of calcium sorbents [2-6], however, none of them was used to the H$_2$S removal. It is not clear with the relationship between the fractal model to sulfur removal activity and it needs to be studied further.

The effect of the calcination of limestone on the fractal dimension and its effect on the sulfidation were investigated through experiment in TGA, which would be benefit for seeking after ideal sulfur removal sorbents with optimum pore distribution. This work claims to enrich the knowledge of the fractal nature of the sulfur removal of limestone under the reducing atmosphere.

II. DETERMINATION OF FRACTAL DIMENSION

Among the numerous methods of the fractal dimension measurement, the nitrogen adsorption is widely used because it is well satisfied with the Hausdorff dimension. Several simple relationships have been proposed as a means of evaluating the fractal dimension from various types of experiments. One of the simplest and most popular relationships is given by FHH equation, which in logarithmic form can be expressed as follows [2, 7-9]:

$$\ln\left(\frac{V_a}{V_m}\right) \propto (D-3)\ln\left(\frac{P_0}{P}\right) \quad (1)$$

Where $D$ is the fractal dimension and $V_a$ is the adsorption volume at the relatively pressure $P/P_0$, $V_m$ is the monolayer capacity, and $P$, $P_0$ is adsorption pressure and the saturation pressure, respectively. According to the adsorption curves, the values of fractal dimension can be derived through the calculation of the slope of the fitting curves, and the detailed process can be referred to our previous work [10].

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### III. RESULTS AND DISCUSSION

#### A. Effect of calcination on the fractal dimension

The calcination of limestones was carried out in TGA instrument, and the detailed procedures can be found in the literature [10]. The mean diameter of limestone particles used in this experiment is 0.23 mm. The fractal dimensions are 2.5 and 2.72, respectively, before and after calcination. It concludes that the calcination has a great effect on the fractal dimension. The inner pore-size distribution in the particles has been varied to a great extent after the calcination and thereafter the sulfidation characteristics. In general, the pore volumes become larger after calcination, the CO\textsubscript{2} emission from the inner particles with hardly any pores results in the appearance of porous structure. However, it will not be necessary that calcination unambiguously leads to the good pore-size structures in terms of the sintering of the particles, and the pore volumes may be compressed, and the small pores may be closed and thereby the specific surface areas and porosity will be decreased. So it is necessary to study the effect of different calcination conditions on the fractal dimension.

1) The effect of calcining temperature on the fractal dimension

In order to investigate the influence of the calcining temperature, the experiment was carried out as the following steps: at first, the furnace of the TGA was purged with CO\textsubscript{2} and the total pressure was raised to 0.5 MPa, then the temperature was increased to the predetermined values where the calcination started. Finally, the gases were changed to the pure N\textsubscript{2} quickly and the calcination began. The calcining temperature was 800-950 °C, and the fractal dimensions obtained at different calcining temperatures are listed in Tab.1.

![Figure 1. Effect of particle size on fractal dimension](image)

**TABLE I. THE TEXTURAL PROPERTIES AND FRACTAL DIMENSIONS UNDER DIFFERENT CALCINING TEMPERATURES**

<table>
<thead>
<tr>
<th>Calcining temperature/°C</th>
<th>800</th>
<th>850</th>
<th>900</th>
<th>950</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area /m\textsuperscript{2}/g</td>
<td>14.7</td>
<td>18.17</td>
<td>16.74</td>
<td>13.2</td>
</tr>
<tr>
<td>Average pore diameter /nm</td>
<td>20.2</td>
<td>15.3</td>
<td>18.5</td>
<td>27.9</td>
</tr>
<tr>
<td>Fractal dimension</td>
<td>2.64</td>
<td>2.72</td>
<td>2.70</td>
<td>2.42</td>
</tr>
</tbody>
</table>

The variation in the calcining temperature will affect the time of full calcination. The sintering of CO\textsubscript{2} in the particles is acknowledged [11, 12], CO\textsubscript{2} can accelerate the sintering. In addition, the time of calcination will influence the calcination process significantly. On the one hand, CO\textsubscript{2} release from the limestone is slower and thus the release time becomes longer at the lower calcining temperature. Therefore, calcination at lower temperature is not optimum. On the other hand, the specific surface areas and pore volumes are larger at higher calcining temperature; however, the particles will sinter at higher temperatures possibly. In a word, the unprimitive pores and thus the largest fractal dimension will be obtained when the calcination occurs at the moderate temperature.

From Tab.1, the largest fractal dimension is obtained at 850°C, which shows that at this temperature the most complex pore distribution forms. And at the highest temperature 950 °C, the smallest fractal dimension which means that the least complex pore distribution formed at this temperature is gained.

The fractal dimension offers a scale-independent, quantitative measure for the degree of surface irregularity. The higher value of fractal dimension, the more irregular the surface and the pores in the particles are, which indicates a larger volume fraction of small pores in the particles. However, the fractal dimension does not reflect the porosity of porous structures quantitatively. According to Tab.1, it can be concluded that the calcination really changes the distribution of pore size. Moreover, we can find that the fractal dimension can relate to the average pore size, as shown in Tab.1. The smaller pore size, the higher fractal dimension is, which denotes that the smaller pores correspond to the more irregular surfaces in the particle.

In addition, it can be seen that the average pore size does not depend on the calcining temperature, which is not well agreed with the literature [12]. They found that the average pore size became larger with the increasing temperature and they thought that the possible reason was as follows: with the increase of calcining temperature, the calcination will proceed drastically, and thus the CO\textsubscript{2} will release quickly, larger volume fraction of large pores in the particles will emerge. Furthermore, the sintering will be more serious at higher calcining temperatures, which makes the small pores into large ones and thus the average pore size becomes larger. Consequently they believed that the fractal dimension will be lower at higher temperatures. Nevertheless, the difference in the experimental conditions, such as the physical property, the equipment and the environment, leads to the seemingly non-conforming results with our present work.

2) Effect of particle size on fractal dimension

The limestone with a particle size 0.055, 0.23 and 0.9 mm were used to be calcined and thereafter used for the sulfidation tests. The fractal dimensions can be obtained for the fully calcined limestones with different particle size at 900°C in N\textsubscript{2} using TGA, as shown in Fig.1.
It is easy to understand that the larger particles, the more time the produced gases escape from the inner surface of the particles need, which increases the sintering of the particles, and the pore-size distribution shifts towards large pore sizes, thus the fractal dimension is low. These results seem not to be in accord with the data in the literature [4], where the authors believed that the smaller particle size, the lower fractal dimension was.

B. Effect of fractal dimension on sulfidation

The reactive gases diffuse through the pore channel to the surface where the sulfidation occurs, and thus the surface structure and pore distribution play an important role in the gases diffusion. The detailed experimental procedures can be found in the literature [10]. The experimental results are shown in Fig.2. The sorbents with similar values of specific surface areas were selected to avoid their effects on the sulfidation, the reaction temperature was 850 °C, total pressure and molar concentration of H2S in the reactive gases were 1MPa and 0.5%, respectively.

According to the Fig.2, the calcined limestones with different fractal dimensions have different sulfur-removal reactivity. The optimum value of 2.70 is corresponding to the highest chemical reaction rate, and for the sorbents with fractal dimension 2.72, the sulfidation rate is not the highest. It can be indicated that the large volume fraction of small pores can form the large surfaces of the pores, but if the small pores exceed an optimum fraction, the possibility of pore blockage will be increased. At the same time, the sintering likes occurring near the small pores. In this sense the large pore size will not produce a perfect sulfidation performance; the samples with too small a fractal dimension will exhibit poor sulfur-removal reactivity on the contrary. And thus, only the calcined limestones with a moderate fractal dimension have a good reaction performance, which is in accord with the literature [5].

Comparing with the two kind of sorbents with different fractal dimension from Tab.1, an interesting phenomenon can be found that the specific surface area of the limestone with fractal dimension 2.72 is larger than that of 2.70. It states clearly that high specific surface area will not probably generate the high sulfur removal efficiency. The most possible reason is that the pore-size distribution in the initial samples before sulfidation shifts towards large pore sizes during the reaction, which decreases the fraction of particle changes due to the chemical reaction and the sintering process, especially for the small pores. Therefore, the specific surface area will not be the only criterion that reflects the sulfur-removal reactivity.

In conclusion, the inner pore structure of sorbents can be evaluated through fractal dimension, and the fractal dimension can be used as a powerful tool to measure the sulfur-removal activity accordingly. The sorbents with either too large or too small fractal dimensions cannot achieve high utilization. Furthermore, the fractal dimension can be used as a valuable ranking index for limestones and is significant to choose the best sulfur-removal sorbents easily.

IV. CONCLUSION

The fractal dimension changes during the calcination of limestones and the relation with sulfur-removal performance were studied in TGA through a global description of irregularities, and the nitrogen adsorption method was used to measure the fractal dimension. The experimental results show that fractal dimension may be a novel method by which the mechanism of gas-solid reaction can be known deeply.

(1) The calcination process affects the structure and the fractal dimensions of the sorbents markedly. With the increase of calcining temperature, the fractal dimensions rise firstly and then diminish. The highest value of fractal dimension 2.72 can be obtained at 850 °C. In addition, the fractal dimension will reduce with the increase of the sorbents particle size gradually.

(2) The fractal dimension of sorbents has a direct influence on the sulfur-removal reactivity. The reactivity of limestones become better with increasing fractal dimensions from 2.42 to 2.70, and when the fractal dimension increases to 2.72, however, the reaction rate seems to be lowered slightly. It can be concluded that the highest reaction rate can be obtained when the calcined limestone has a moderate fractal dimension of 2.70.

REFERENCES


