FULL PAPER

Preparation the porous ceramic for flue gas adsorption by microwave treatment of industrial waste

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In this paper, the influence of different microwave conditions on industrial waste residue was studied. It is hoped that the porous ceramic materials which can absorb SO₂ and NOₓ in flue gas efficiently can be prepared by using these industrial waste residues. The results show that microwave treatment can effectively improve the activity of industrial waste residue and the adsorption capacity of flue gas. And the appropriate microwave sintering power and sintering time can improve the specific surface area and pore size of adsorbent, and enhance the adsorption capacity of flue gas. Under the experimental conditions, the best microwave sintering conditions are sintering power 1000 W and sintering time 1200 s. Under these conditions, the porous ceramic adsorbent has the best adsorption effect, with the desulfurization rate of 98.8% and the denitration rate of 91.9%.

Key-words : Industrial waste, Microwave, Porous ceramics, Desulfurization, Denitration

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1. Introduction

Air pollution has been the focus of attention in recent years. The SO₂ and NOₓ as the main gases of air pollution, how to control and reduce the emission concentration has been a research hotspot.¹,² Taking the sintering and pelletizing processes in metallurgy as an example, the main pollutants emitted are SO₂ and NOₓ, which account for 79 and 50% of the total metallurgical process respectively.³

At present, the main flue gas purification technologies include activated carbon (coke) adsorption and flue gas catalytic oxidation.⁴⁻⁸ In these methods, the materials used are not only chemical raw materials and industrial reagents, but also the removal process is relatively cumbersome. When enterprises use these technologies, the production cost of enterprises will increase significantly. And the high cost also seriously limits the widespread of these flue gas purification technologies. Therefore, how to develop a low-cost flue gas adsorption material and purification technology seems to be of great significance.

Nowadays, with the decrease of natural resources, more and more researches have been carried out on how to deal with and utilize the waste resources in an efficient way.⁹,¹⁰ In China, a lot of industrial waste is produced every year. Such as fly ash, carbide slag, and refining waste slag, et al. There are a lot of strong alkaline substances in these waste slags. These strong alkaline substances not only have great potential in the treatment of these flue gases (SO₂ and NOₓ), but also some metal oxides contained in these wastes will play a catalytic role in the adsorption and reaction process.¹¹⁻¹⁴

If these wastes can be reasonably treated and prepared into flue gas adsorption materials, both the flue gas purification can be realized and the resources of waste treatment can be reused.¹¹⁻¹⁴ However, when these wastes are recycled, the phenomenon of agglomeration is relatively serious and the chemical activity is relatively low. If we want to make better use of these wastes to prepare the high-efficiency flue gas adsorbents, we must modify these wastes to improve their reactivity and adsorption performance.

Conventional heating is prone to localized heating of the gas and coal combustion brings secondary pollution, which is contrary to the concept of sustainable development. As a clean energy source, microwave can achieve the purpose of high efficiency and uniform heating from inside to outside.¹⁵,¹⁶ Replacing coal-fired heating with microwave heating can not only avoid secondary smoke pollution but also save lots of energy and promote the sustainable development of ecological environment. In addition, microwave can stimulate the energy of gas molecules.¹⁷,¹⁸ Ma et al. studied the denitrification of activated carbon modified by microwave, but the effect of microwave on gas molecules was not involved.¹⁹,²⁰

Inspired by the results above, in this paper, the microwave as the special treatment method is applied to the comprehensive treatment of these industrial wastes. It is hoped that after microwave modification and microwave sintering, a new efficient porous ceramic material for flue gas adsorption can be obtained.

2. Experimental

2.1 Experimental materials

In this experiment, all the raw materials are from factory

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waste. The chemical compositions of the fly ash, carbide slag, and refining slag are shown in Table 1. Its corresponding X-ray diffraction (XRD) profile is shown in Fig. 1, which indicates that fly ash contains partially imperfect combustion of char and a large amount of calcium hydroxide and some calcium peroxide with strong oxidizing properties exists in carbide slag. Calcium oxide exists as a polymer in refining slag. Its corresponding XRD profile is shown in Fig. 1, which indicates that fly ash contains partially imperfect combustion of char and a large amount of calcium hydroxide and some calcium peroxide with strong oxidizing properties exists in carbide slag. Calcium oxide exists as a polymer in refining slag. Elements such as Si, Al, and Mg in raw materials can provide active sites for SO₂ or NO adsorption.

2.2 Experimental methods
In the course of the experiment, the sample preparation method and process are shown in Fig. 2. First, all raw materials are crushed and ground to within 0.075 mm. After that, fly ash and carbide slag were mixed in the proportion of 1:1 respectively. Then the samples were modified by microwave (JuYuan, China, WBMW-GS2) with low power to improve the reactivity of the raw materials. Its microwave power is 200 W and the modification time is 1200s. After modification, the materials will be rehydrated. The hydration time is 12 h. In the process of hydration, the method of heating and stirring in the water bath is used to ensure complete reaction. After the completion of the water bath, dry the hydrated sample to constant weight. Then the dried sample and the refining slag are mixed in the ratio of 2:1 for the second time. After mixing, the mixture is pressed into a cylindrical adsorbent with a diameter of 20 mm and a height of 3 mm through a mold, and the pressing pressure is 100 MPa. Finally, the pressed samples are sent to the microwave generator for sintering. Meanwhile, we also use scanning electron microscope (Hitachi, Japan, S-4800 II), XRD (Brook, Germany, D8 ADVANCE), BET (Cona, American, iQ2, Autosorb) and flue gas adsorption experiments to detect and analyze the porous ceramic adsorbents under different conditions. Then the influence of different microwave treatment conditions on the adsorbent and the best preparation scheme of the adsorbent are revealed.

3. Results
3.1 Change after microwave modification and hydration
It can be seen from Fig. 3(a) that the surface morphology and packing structure of the initial mixture particles of fly ash and carbide slag are relatively denser than the surface morphology and packing structure after modification and hydration. At the same time, due to the agglomeration of raw materials, the surface coarseness of these particles is also small. After low-power microwave modification, the non-thermal effect of microwave makes the energy stored in the mixture increase, resulting in the fracture of aggregates and chemical bonds. Therefore, it can be found after modification [Fig. 3(b)], there are a lot of cracks on the surface of modified particles, and the surface morphology also shows scales. After modification, the surface morphology and packing structure of the mix-
ture particles have been significantly improved than that before modification. These beneficial effects will also improve the loose packing of the materials’ structure. So that these modified adsorbent particles are not only conducive to the improvement of the subsequent hydration effect but also improve the reactivity of raw materials (especially for fly ash). After the modified samples are fully hydrated and dried, as shown in Fig. 3(c), the porosity and coarseness of the raw material's packing and connecting structure are further improved due to the hydration reaction of alkali metals and their oxides. After hydration, the samples are porous, and there are a lot of micropores and mesopores inside. Significantly, in the process of flue gas adsorption, the increase of micropores and mesopores can effectively improve the efficiency of physical and chemical adsorption.

3.2 Change of the adsorbent after microwave sintering

It can be seen from Fig. 4(a) that the whole adsorbent material will become dense again when it is pressed. However, in the process of microwave sintering, the dense state of adsorbent material will disappear quickly due to the joint action of the thermal effect and non-thermal effect of the microwave. On the one hand, due to the thermal effect of the microwave, the water molecules adsorbed and crystallized in the hydration process of the adsorbent will continuously overflow from the inside of the adsorbent under the action of the microwave. The loss of water molecules will produce a lot of pores in the adsorbent. On the other hand, due to the non-thermal effect of the microwave, the agglomerates and chemical bonds in the adsorbent will further fracture to form more micro pores and

Fig. 3. Morphology and structure changes of adsorbent after microwave modification and hydration.

Fig. 4. Morphology and structure changes of materials after microwave sintering.
fractures. The increase of micropores and fractures will increase the specific surface area of the adsorbent again, and enhance the retention time and contact probability of flue gas during the adsorption process. These gains will enhance the adsorption effect of flue gas. At the same time, in the process of microwave sintering, due to the effect of thermal effect, the carbon element from the fly ash will be consumed continuously and generate a lot of heat. The heat energy is conducive to the good connection and sintering of the adsorbent itself and the pores formed, and to the strengthening of the stability of the adsorbent itself [as shown in Fig. 4(c)]. However, if the sintering time is too long or power is too large, the amount of liquid phase formed by the adsorbent itself will also increase. And under the condition of over sintering, the pores in the adsorbent will be filled by these liquid-phase materials. Finally, become a dense material [Fig. 4(d)].

3.3 Flue gas adsorption effect under different conditions

In order to explore the effect of different microwave sintering conditions on flue gas adsorption, the porous adsorbent obtained under different conditions was tested for flue gas adsorption, and the results are shown in Fig. 6. During the test, the compositions of flue gas used in the experiment were SO$_2$ 550 mg/m$^3$, NO 300 mg/m$^3$ and N$_2$ was equilibrium gas. The SO$_2$ and NO concentrations before and after passing through the microwave tube furnace were measured by flue gas analyzer (FGA 10 Gas Analyzer).

It can be seen from Fig. 5 that the changing trend of flue gas adsorption effect is basically the same for both the desulfurization process and the denitrification process. Compared with the adsorption material without microwave sintering, microwave sintering can effectively improve the adsorption capacity of the adsorbent itself. With the increase of microwave power and time, the adsorption effect of the adsorbent itself is also improved. This is also consistent with the former analysis of the structural change of the adsorbent, that is, in the process of microwave sintering, a large number of micropores, mesopores, and cracks will appear in the adsorbent, which will improve the physical adsorption capacity. At the same time, the alkaline substances are gradually dehydrated and reduced, so that the chemical adsorption effect is also improved. However, when the microwave power is too large or the sintering time is too long, the micropores and mesopores in the adsorbent will be filled by the newly formed sintering liquid phase, resulting in the reduction of its own porosity, and ultimately affecting the adsorption effect. Under the experimental conditions, the best microwave sintering conditions are sintering power 1000 W and sintering time 1200 s. Under these conditions, the porous ceramic adsorbent has the best adsorption effect, with the desulfurization rate of 98.8% and the denitrification rate of 91.9%.
4. Discussion

4.1 Flue gas adsorption principle of the porous ceramic adsorbent

The adsorption of SO₂ and NO in the flue gas by the adsorbent is mainly divided into three processes (as shown in Fig. 6). The first stage, surface adsorption, that is, SO₂ and NO molecules are diffused from the outside to the surface of the adsorbent particles. The second stage, indiffusion, the SO₂ and NO diffused from the surface to the inside of the adsorbent particles and diffused in the inner pore structure. The final stage, chemical adsorption, the SO₂ and NO molecules reacted with alkaline components such as CaO in the adsorbent and produced sulfates and nitrates under the strong oxidation of CaO₂. Among the above three stages, that with the greatest resistance would become the main speed control link of the adsorption rate in the adsorption process.

4.2 Specific surface area and aperture analysis

Table 2 shows the results of specific surface area and pore volume of adsorbent under different conditions. It can be seen from samples 1# and 2# that with the increase of sintering power, the area of micropore increases about 4 times, while with the further increase of sintering power (3#), the area of micropore decreases about 98%. At the same time, it can be seen from samples 2# and 4# that the specific surface area of the adsorbent decreases about 33% when the sintering time is continuously extended, and about 65% when the sintering time is further extended (5#). It can be seen that the proper sintering time and power can effectively improve the specific surface area and pore volume of the adsorbent. Especially for the microporous area and volume of adsorbent, it is one of the fundamental reasons that affect the adsorption performance of adsorbent.

Figure 7 shows the pore size distribution of adsorbent under different conditions. It can be seen from Fig. 7 that the mesoporous pore size distribution curve of adsorbents prepared under different microwave power or sintering time has a single and wide peak. It shows that there are many mesopores in the adsorbent after microwave sintering. However, for the most probable pore size, the most probable pore size is relatively largest when the microwave power is 1000 W and the sintering time is 1200 s. At this time, the most probable pore size can reach 22.76 nm.

4.3 Change of the adsorbent after adsorption

Figure 8 shows the micromorphology and composition of the porous ceramic adsorbent after flue gas adsorption. Compared with Fig. 4(c), the morphology of the adsorbent did not change significantly after flue gas adsorption. The specific surface area and porosity of the material are still high, and the inner micropores, mesopores, and cracks are still clearly visible. It was found that S and N appeared in the elements on the surface of the adsorbent after adsorption, which indicated that the adsorbent could effectively react with SO₂ and NO in the flue gas during the adsorption process. Finally, the purpose of flue gas adsorption and purification is achieved.

Figure 9 shows some main phase composition changes of adsorbent before and after microwave sintering and after adsorption test. It can be seen from Fig. 9 that the composition of raw materials is relatively complex, so the

| Sample | Sintering conditions | Specific surface area /m²·g⁻¹ | Micropore area /m²·g⁻¹ | Pore volume /cm³·g⁻¹ | Micropore volume /cm³·g⁻¹ |
|--------|----------------------|-------------------------------|------------------------|----------------------|--------------------------|
| 1#     | 500 W, 20 min        | 8.8924                        | 0.5921                 | 0.05108              | 0.00030                  |
| 2#     | 1000 W, 20 min       | 8.5041                        | 2.4706                 | 0.04888              | 0.00132                  |
| 3#     | 1500 W, 20 min       | 9.4146                        | 0.0544                 | 0.04456              | 0.00003                  |
| 4#     | 1000 W, 10 min       | 12.7153                       | 0.8565                 | 0.06888              | 0.00044                  |
| 5#     | 1000 W, 30 min       | 2.9522                        | 0.7483                 | 0.01768              | 0.00045                  |

Fig. 7. Mesoporous pore size distribution under different conditions.

(a) Different power

(b) Different time
The main phase composition will not change significantly after microwave sintering. After microwave sintering, although the phase composition after the preparation of adsorbent is relatively more. After microwave sintering, although the main phase composition will not change significantly. However, with the loss of crystal water, adsorbed water and the consolidation of sintering, the intensity of the adsorbent phase characteristics can be strengthened. Therefore, the phase composition after sintering is clearer and the consolidation of sintering, the intensity of the adsorption reaction in the adsorption material. This is in accordance with the results of the former analysis. The flue gas adsorbent prepared by microwave treatment of industrial waste has good chemical adsorption capacity.

5. Conclusion

1) Compared with the adsorption materials without microwave treatment, microwave treatment can effectively improve the activity of industrial waste residue and the adsorption capacity of flue gas.

2) Appropriate microwave sintering power and sintering time can improve the specific surface area and pore size of adsorbent, and enhance the adsorption capacity of flue gas.

3) Under the experimental conditions, the best microwave sintering conditions are sintering power 1000 W and sintering time 1200 s. Under these conditions, the porous ceramic adsorbent has the best adsorption effect, with the desulfurization rate of 98.8% and the denitrification rate of 91.9%.

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Conflicts of Interest The authors declare that there are no potential conflicts of interest regarding the publication of this article.

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