Experiment and Mechanism Analysis of Desulfurization with a MgO-Based Desulfurizer Fixed Bed Method

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ABSTRACT: To reduce the cost of the current commercial desulfurization and eliminate effluents, the MgO-based desulfurizer fixed bed desulfurization tests were carried out in a dry environment. By means of X-ray diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy, the absorption effects of the MgO-based desulfurizer on SO₂ were thoroughly investigated. Physical and chemical analyses show that most of the SO₂ diffused on the desulfurizer surface was oxidized into sulfate and some SO₂ entered the inner hole and the microhole of the desulfurizer. The technology was applied to sintering flue gas and achieved 97% stable desulfurization at low temperatures, which indicates that the MgO-based desulfurizer has obvious industrial competitive advantages.

1. INTRODUCTION

At present, the most widely used desulfurization technology is the wet limestone gypsum method (FGD), which belongs to wet desulfurization. The method is usually used in large power plants and popularized in flue gas desulfurization of sintering flue gas and industrial boilers. FGD uses a limestone slurry to absorb SO₂ in flue gas and reacts to form calcium sulfite. The method has a relatively high desulfurization efficiency, but the calcium sulfate produced by the method causes equipment fouling and the calcium chloride generated by Cl⁻−Ca₂⁺ in the flue gas causes corrosion to equipment.¹ To improve the defect, Yang et al. have recently shown some improved FGD and semidry techniques.²

In all methods, a wet magnesium oxide method is developed and popularized. Wet magnesium oxide is the reaction of MgO and water to produce a magnesium hydroxide slurry for flue gas desulfurization. This method has a high efficiency and does not clog the device but the desulfurization effluents are large and difficult to deal with. It is necessary to find a desulfurization method without secondary pollutants.

For an adsorption system, it is very important to select the adsorption material correctly. Metal oxides have gained wide attention and have been applied in many fields. SO₂ is an acid anhydride which is susceptible for reaction with alkaline substances. Jun et al. showed that MgO and CaO were commonly used for removing sulfur dioxide.³ Feng et al. have shown that metal oxide surfaces have special properties and remove SO₂ by loading on other porous materials or synergistic effects of various metals.⁴ Shen et al. have studied the oxidation kinetics of sulfites in the process of wet flue gas desulfurization by magnesium oxide, the study showed that the MgO-based wet flue gas desulfurization system is of industrial reference value.⁵ Nevertheless, desulfurization under wet conditions will produce effluents. Rodriguez et al. have studied a {Na + SO₂}/MgO system, from the results of the S 2p photoemission spectra for the adsorption of SO₂ on MgO, they pointed out that MgO can absorb SO₂ but no chemical reaction or dissociation of SO₂ occurs.⁶ Baranov et al. and Grigorov used MgO as a substrate for the epitaxial growth of multilayer and clusters.⁷ Pacchioni et al. explored the possibility of the MgO and SO₂ reaction from the perspective of the vibrational modes and the core level binding energies.⁸ It is well known that surface defects also have special properties. As a kind of NaCl crystal structure, MgO has Schottky defects on its surface, which makes it catalytic and have adsorption properties. Some learners studied the adsorption properties and characteristics of SO₂ on the Li atom deposited on the surfaces of metal oxide MgO(100) on both defect (F-center) and anionic sites.⁹ In addition, to explore the role of SO₂ on the surface of the magnesium oxide composite material or single crystal of magnesium oxide, Czyżewski and Fang et al. used various surface science techniques, in particular infrared pectroscopy, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy.¹⁰ The versatility of MgO is linked to its structure and relatively well-defined surface chemistry. The
above has a significant implication, it allows the utilization of MgO for SO2 removal under a dry environment. However, few studies have been applied to actual sintering flue gas, so it is still necessary to supplement the data.

In this paper, the absorption of SO2 by the MgO-based desulfurizer under a dry condition is introduced. The actual sintering flue gas is tested and the adsorption mechanism of SO2 is discussed. The results show that the process has a low failure rate and reliable operation for industrial desulfurization with higher environmental protection standards.

2. RESULTS AND DISCUSSION

2.1. Scanning Electron Microscopy Studies. To explore the change of the surface morphology of desulfurizers (before and after desulfurization), sampling I (fresh desulfurizer which unabsorbed SO2), sampling II (desulfurizer which was at the outlet and absorbed SO2), and sampling III (desulfurizer which was at the inlet and absorbed SO2) were analyzed by scanning electron microscopy (SEM). The SEM micrographs (×5000) of desulfurizers are shown (Figure 1). It can be seen that sampling I had a smooth surface with some scaly particles. Sample II was coarser than sample I, with a large number of scaly surfaces. Sample III had a granular aggregate, almost no smooth surface.

Sample I’s surface was the smoothest among the three, followed by sample II and III. The difference in morphology of the three samples is due to the absorption of SO2 and the location of the desulfurizer. Sample I is compared with II, a new scaly surface was the sign of the desulfurizer absorbing SO2, and the scaly surface was associated with the formation of the product. Comparing sample II and III, the surface of sample III was much rougher than sample II. This indicates that at the same desulfurization time, more products were deposited on the surface of the desulfurizer at the reactor’s inlet than the outlet. In conclusion, a scaly morphology (the sample II) was the result of the product layer formed in the early stages, a granular aggregate morphology (the sample III) was the diffusion of SO2 and the formation of new products on the product layer. According to the SEM micrographs, the products accumulated on the surface of the desulfurizer and formed a solid product layer, which indicates that the desulfurizer had chemically absorbed SO2. According to relevant studies, MgSO4 can be formed on the surface of MgO to form a solid product layer, SO2 will gradually diffuse on the product layer and form a new MgSO4.10 The SEM analysis reflects the change of the product layer, but whether SO2 was absorbed into the inner hole of the desulfurizer and caused a chemical reaction needs further study.

2.2. X-ray Diffraction Studies. The powder X-ray diffraction (PXRD) of the fresh desulfurizer and the after desulfurizer were recorded and shown in Figure 2. We can see in 2θ, 18.6, 38.022, and 50.865 are obviously positions of the Mg(OH)2 crystal structure (Figure 2) and 29.572 and 30.102 are the positions of the MgSO4 crystal structure (Figure 2b). XRD patterns measured for the fresh and the after desulfurizer in a dry condition, we can see that the diffraction spectrum of the desulfurizers was very similar to that of Mg(OH)2, SiO2, MgCa(CO3)2, and MgCO3, while there was a small amount of MgSO4 in the after desulfurizer. Whereas there were no significant sulites, which is consistent with the literature from Czyzewski.11 By combining the analyses of SEM and XRD, the product obtained was magnesium sulfate, but the formation of the product was less in the internal structure of the desulfurizer. The product layer was most likely on the surface of the
desulfurizer. We confirm that it can be explained by the theory of spontaneous monolayer dispersion. In the phase analysis of many industrial catalysts, it is found that when a catalyst with a high specific surface area is loaded with oxides or salts the crystal peak of the active component cannot be found even if the content is very high. The biggest possibility of this phenomenon is that the active components exist in a single dispersed form on the surface of the carrier. Active components are usually spontaneously dispersed to the surface of the carrier in a single or sub-monolayer manner by the surface diffusion mechanism. Although it is a single-layer coverage, its load can be very high.

We performed XPS analysis on sample III.

2.3. XPS Studies. The XPS tests were performed for the sulfur element on the surface of the desulfurizer. XPS is a surface analysis with a detection depth of 5–10 nm. The test results are shown, SO$_2^{2−}$ (170–169 eV) was obviously present, no signal indicate that SO$_3^{2−}$ (168–167 eV) and S (163.5–161.5 eV) were present (Figure 3). This indicates that sulfate products were indeed deposited on the surface of the desulfurizer and the oxidation of SO$_2$ occurred instead of reducing SO$_2$ to S (SO$_2$$_{gas}$ → S$_{ads}$ + O$_{ads}$). The surface of the MgO-type desulfurizer has the feature of Schottky defect, such that SO$_2$ can react with the O$_{2−}$ (oxygen defect site) on the desulfurizer surface. According to the characteristics of Schottky defects, the process can form strong surface bonds on the surface of the carrier, similar to ionic bonds. The process had little change in enthalpy when the disorder degree increases. It was a thermodynamic spontaneous process, so it was easy to be performed without a high temperature and other conditions. Although the XPS test shows no signal of SO$_3^{2−}$, we believe that SO$_2$ was not directly oxidized to SO$_3^{2−}$. In conclusion, SO$_2$ was first oxidized to SO$_2^{2−}$ at the oxygen defect site (O$_{2−}$) on the surface of MgO, while SO$_2^{2−}$ was weakly bound to the oxygen defect site on its surface, it was easily oxidized to SO$_3^{2−}$ by O$_2$ in the flue gas.

The peak shape of Mg(OH)$_2$ existing by prolonged exposure to air. Apparently, the carbonate was formed because of the action of CO$_2$ naturally present in air on CaO or Ca(OH)$_2$ contained in the sorbent material. It was probably because the sample was exposed to the atmosphere during handling, powdering, and measuring of XRD patterns.

The desulfurization process was as follows: SO$_2$ reacted redox reactions with the oxygen defect on the surface of the MgO-based desulfurizer to produce SO$_3^{2−}$. Afterward, O$_2$ in the flue gas further reacted with SO$_3^{2−}$ to produce SO$_4^{2−}$. Mechanism of the reaction: SO$_2$($g$) + O$_2^{2−}$ → SO$_3^{2−}$ → SO$_4^{2−}$.

Chemical reaction on the desulfurizer

\[ \text{MgO} + \text{SO}_2 = \text{MgSO}_3 \]
\[ \text{MgSO}_3 + \frac{1}{2} \text{O}_2 = \text{MgSO}_4 \]
\[ \text{MgO} + \text{H}_2\text{O} = \text{Mg(OH)}_2 \]
\[ \text{Mg(OH)}_2 + \text{SO}_2 + \text{O}_2 = \text{MgSO}_4(\text{OH})_2 \]

The reaction products of MgO and SO$_2$ were different under different conditions. As research showed that materials with both calcium and magnesium produced the CaSO$_4$$\_3$MgSO$_4$ phase after sulfating, and no single CaSO$_4$ or MgSO$_4$ phase was produced. According to the research results of Pacchioni et al., though no pure MgSO$_4$ phase was detected by X-ray, on the MgO surface, SO$_2$ formed weakly bound surface complexes which can also achieve desulfurization.

According to the study by Sun et al., most gas–solid noncatalytic reactions presented two process. The first stage had a fast reaction rate, which was because of the chemisorption. The second stage showed a platform, as the product was covered on the material surface and within the pore structure. The reaction rate of the second stage was limited by the material consumption and product coverage of the first stage. Combining the information, different from the fresh desulfurizer, the surface morphology of the desulfurizer after a long-period reaction assuredly changed (Figure 1). We believe that the reaction products were deposited on the desulfurizer surface after the first stage; SO$_2$ began to diffuse and transfer mass in the pore structure and formed a solid product layer as the reaction progressed. Energy-dispersive X-ray spectroscopy (EDS) was used for the elemental analysis of the samples. The effect of SO$_2$ on the desulfurizer after a long-period reaction is proved (Table 1). Table 1. Results of EDS Element Analysis

| atomic percentage | Mg % | O % | S % | Si % | Ca % | Fe % |
|------------------|------|-----|-----|------|------|------|
| I                | 59.88| 29.43| 0   | 3.72 | 0.1  | 0.13 |
| III              | 47.39| 24.46| 2.95| 0.77 | 4.13 | 0.31 |

and Fe was mainly caused by their small content in the desulfurizer and the uneven desulfurizer itself, but it can be fully proved that sample III contains the sulfur elements.

In addition, some studies have also suggested that the solid product, MgSO$_4$ will form on the surface of MgO, and with the formation of the solid product layer, SO$_2$ will begin to diffuse in the solid product layer and form new MgSO$_4$. The corresponding SEM micrographs of the solid product layers showed scaly particles, scaly surfaces, and granular aggregate. As we known from the image, the MgO substrate is smooth. This is consistent with the SEM micrographs of the present study, sample I’s surface was one of the smoothest among the three (Figure 1). Sample II possessed a SO$_2$ quantity smaller than that of sample III, sample II’s morphology of scaly surfaces is because the product layer began to form, the morphology of sample III appeared as a granular aggregate because the SO$_2$ in the product layer continued to spread.

The above experimental results have great application potential, so engineering applications were carried out.
The test was arranged behind sintering pellet production line’s dust collector and in front of the stack of the plant. A bypass flue gas was drawn out from the dust collector, and the flow rate was about 500 m$^3$/h. The circular particles of the desulfurizer with a diameter of 3–5 mm, perpendicular to the windward surface, were installed in the box in the form of multiple layers (separated by a plate with holes) to desulfurize the flue gas. We observed three days of sulfur removal, the test results show that the MgO-based desulfurizer could effectively and stably desulfurize the actual sintering flue gas under the condition of no water. When the SO$_2$ concentration of the imported flue gas was about 170 mg/m$^3$, after the action of the MgO-based desulfurizer, the SO$_2$ concentration of the exported flue gas was reduced to 3 mg/m$^3$, the desulfurization rate of the MgO-based desulfurizer was up to 98%. In addition, according to the test results of NO import and export, the desulfurizer also had a certain removal effect on NO, and the removal rate of NO was about 20%. Indeed, Ma et al. have shown that the presence of SO$_2$ can promote the absorption of nitrogen oxides on the surface of MgO.$^{20}$ Further studies on industrial application and industrial design will be summarized in our next study.

2.4. Stability Test. Desulfurization experiments with a cycle of 15 days and 30 days were conducted, and the desulfurization efficiency is shown in Figure 4. The desulfurization efficiency was stable at 97% for the operation of 15 days (Figure 4a), and the desulfurization efficiency of the MgO-based desulfurizer was still high after the operation of 30 days, and the efficiency was stable at 97% for the whole cycle (Figure 4b). The sudden drop in efficiency on day 6 was related to the operation of the plant (Figure 4b). The desulfurization efficiency was slightly reduced to 95% on day 28–30, which might be due to the long operation time, so the MgO-based desulfurizer showed a slight desulfurization saturation. At present, the desulfurization efficiency of FGD, which is commonly used in the industry, can reach 90%, but the stability of its efficiency is still affected by the original flue gas parameters and equipment operation mode. Compared with FGD, the MgO-based desulfurizer fixed bed method can ensure high efficiency and better stability.

The above experimental results show that the desulfurization rate of the MgO-based desulfurizer was fast and the efficiency could reach 97% within 1 h, which was due to the formation and deposition of the product layer on the desulfurizer surface (Figure 1). According to the XPS analysis, the product was sulfate (Figure 3). From the XRD and XPS patterns (Figures 2 and 3), the product layer was formed only on the surface of the desulfurizer. From the above, SO$_2$ was adsorbed on the surface of the desulfurizer, and the sulfate product layer was formed by chemical adsorption. With the progress of the desulfurization, most of the SO$_2$ diffused in the product layer.

3. CONCLUSIONS

This study presents a method to remove SO$_2$ from the sintering flue gas in a dry environment and explores the mechanism of the action between the MgO-based desulfurizer and SO$_2$. The conclusions are:

(1) In the whole process, the gas phase of SO$_2$ first diffused on the surface of the MgO-based desulfurizer. The oxygen defect position of SO$_2$ on the surface of the desulfurizer was oxidized into MgSO$_3$. Meanwhile, MgSO$_3$ reacted with O$_2$ in the flue gas to generate MgSO$_4$ products.

(2) A few SO$_2$ molecules could enter the inner pores and micropores of the MgO-based desulfurizer to form MgSO$_4$ products, most of the products were deposited on the surface of the desulfurizer.

(3) MgSO$_4$ formed a product layer which was dispersed on the adsorbed material surface and inner pore at the same time. With the extension of the reaction time, the amount of MgSO$_4$ would gradually increase, and the product layer gradually showed the appearance of scales, aggregates, and gullies.

We have found that the method can remove SO$_2$ efficiently and stably. The desulfurization efficiency of the MgO-based desulfurizer was up to 97% after 15 days of operation and 94% after 30 days of operation. With low cost and no secondary pollution, the technology has potential for application in industrial gas and can be applied for the desulfurization of flue gas from coal-fired boilers, gas-fired boilers, oil-fired boilers, sintered pellets, electrolytic aluminum, building materials, and so forth.
4. EXPERIMENTAL SECTION

4.1. Scanning Electron Microscopy−Energy-Dispersive X-ray Spectroscopy. The morphologies of the MgO-based desulfurizer were observed by a ULTRA PLUS, Zeiss microscope (Germany) Co., LTD. EDS (Mg, S, Ca, and Fe content) was performed using an elemental analyzer (Vario-EL).

4.2. X-ray Diffraction. XRD patterns were recorded on a Panaco diffractometer (Netherlands), with the Cu Kα radiation (\( k = 1.54056 \) Å) in the range of 2\( \theta \) = 10°−90°, step length 0.02.

4.3. XPS Study. The XPS spectra presented were measured using an Al K Alpha source with a Scienta SES 2002 spectrometer operating at constant transmission energy (\( E_p = 30 \) eV).

The designation of these desulfurizers throughout the test is the fresh desulfurizer (unabsorbed SO\(_2\)) and after desulfurizer (absorbed SO\(_2\)), respectively. Both the fresh desulfurizer and the after desulfurizer were studied. The samples after experiments (described below) were chosen for characterization.

4.4. Preparation of the MgO-Based Desulfurizer. Magnesium oxide was matured at 70 °C for 2 h to form a magnesium hydroxide slurry. The magnesium oxide dry powder (90 wt %) and magnesium hydroxide slurry (10 wt %) were evenly stirred to granulate by rolling balls. Circular grains with a particle size of 3−5 mm was produced by using the disk granulation mechanism at room temperature and pressure. They were used after being placed at room temperature for 2 h. Sealed storage to prevent CO\(_2\) from reacting with Mg(OH)\(_2\). The main composition and content of the raw materials were magnesia (91.85 wt %), silica (6.80 wt %), calcium oxide (0.86 wt %), and ferric oxide (0.49 wt %). Through the special processing, it was fully mixed and processed to 3−5 mm round grains.

4.5. Performance Tests. The experiments for the removal of SO\(_2\) were carried out in a desulfurization tower (1200 mm high with a diameter of 180 mm) at room temperature and pressure. Steel plates with holes were placed at the bottom of the desulfurization tower to support a measured amount of the MgO-based desulfurizer. The MgO-based desulfurizer was purged in situ by passing N\(_2\) for 30 min at the reaction temperature. The tests of the activity were performed with a mixture of SO\(_2\) (60 ppm), NO (90 ppm), CO (5 vol %), CO\(_2\) (15 vol %), and O\(_2\) (20 vol %) balanced by N\(_2\), for which the total intake flow was 1800 L/min. A flue gas analyzer (Lao Ying 3012H) was used for online monitoring the concentrations of SO\(_2\) in the outlet gas. The desulfurization schematic diagram is shown in Figure 5. For the convenience of measurement in the
actual sintering site, the reactor was actually divided into four sections (Figure 6). The SO$_2$ conversion was calculated according to the following formula

$$\text{SO}_2\text{ conversion} = \frac{C_{\text{SO}_2,\text{inlet}} - C_{\text{SO}_2,\text{outlet}}}{C_{\text{SO}_2,\text{inlet}}} \times 100\%$$

where $C_{\text{SO}_2,\text{inlet}}$ refers to the concentration of SO$_2$ at the inlet of the desulfurization tower and $C_{\text{SO}_2,\text{outlet}}$ refers to the concentration of SO$_2$ at the outlet of the desulfurization tower.

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**Notes**

The authors declare no competing financial interest.

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