ABSTRACT: Steel slag is a calcium-containing alkaline industrial solid waste that can replace limestone for flue gas desulfurization. It can remove SO₂ and coproduce silica gel while avoiding CO₂ emission from limestone in the desulfurization process. In this study, steel slag with a D₅₀ of 3.15 μm was used to remove SO₂. At room temperature, with a solid−liquid ratio of 1:10, a stirring speed of 800 rpm, and the mixed gas introduced at a flow rate of 0.8 mL/min, 1 ton of steel slag could remove 406.7 kg of SO₂, a SO₂ removal efficiency typical of existing calcium-rich desulfurizers. As limestone desulfurization can release CO₂, when limestone desulfurization was replaced with steel slag of equal desulfurization ratio, CO₂ emissions could be reduced by 279.6 kg and limestone could be reduced by 635.5 kg. The yield of silica gel was 5.1%. Silica gel pore structure parameters were close to those of commercially available B silica gel. Products after desulfurization were mainly CaSO₄·2H₂O, CaSO₄·0.5H₂O, CaSO₃·0.5H₂O, and silica gel. With a silica gel dosage of 30 mg, a temperature of 20 °C, a pH value of 6.00, a stirring time of 0.5 h, and a methylene blue concentration of 0.020 mg/mL, the removal ratio of methylene blue adsorbed by silica gel was 98.4%.

1. INTRODUCTION

Nearly 100 desulfurization processes have been developed, but fewer than 10 have been applied industrially. Among the desulfurization systems in operation or under construction, wet flue gas desulfurization accounts for ~80%. Among wet flue gas desulfurization technologies, limestone/lime-gypsum is the most widely used and mature standard desulfurization process technology worldwide. It is the basic process for flue gas desulfurization in large-unit thermal power plants.

Cheap and readily available limestone or lime was used as a desulfurization absorbent in this method. Limestone is crushed and ground into powder and mixed with water to form an absorbent slurry. When lime is used as the absorbent, lime powder is digested and water is added to make the slurry. In the absorption tower, the absorption slurry contacts and mixes with the flue gas. SO₂ in flue gas, calcium carbonate in slurry, and the blown oxidizing air undergo a chemical reaction, and the final reaction product is desulfurization gypsum. Small droplets are removed from flue gas by a mist eliminator after desulfurization, heated by a heat exchanger, and discharged into a chimney. The desulfurized gypsum slurry is recovered after being dehydrated by a dehydration device.

When limestone is used as the absorbent, SO₂ is converted in the absorption tower, and the reaction equation is as follows

\[ \text{CaCO}_3 + 2\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(HSO}_3)_2 + \text{CO}_2 \]  

Herein, the slurry containing CaCO₃ scrubbing suspension is sprayed into the flue gas from the upper part of the absorption tower. In the absorption tower, SO₂ is absorbed to generate Ca(HSO₃)₂, which falls into the absorption tower slurry tank. The blown air causes calcium bisulfite to be oxidized into gypsum in the absorption tower slurry tank.

\[ \text{Ca(HSO}_3)_2 + \text{O}_2 + \text{CaCO}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{CO}_2 \]  

Thus, limestone/lime-gypsum wet flue gas desulfurization (WFGD) consumes a large amount of natural minerals, limestone, and lime and also releases greenhouse gas CO₂. Therefore, based on the “carbon peak, carbon neutrality” vision, it is important to develop a desulfurization agent that can replace natural ore without emitting other pollutants. According to reports, CO₂ emitted by thermal power plants accounts for about 33−40% of global emissions. When 1 ton of limestone

Received: March 27, 2022  
Accepted: May 27, 2022  
Published: June 9, 2022
Steel slag (SS) is a solid waste that is produced in the steelmaking process. In 2018, China produced nearly 100 million tons of SS, which accounts for nearly 50% of the global SS production. However, nearly 70% of SS was stacked in a disorderly manner, which will inevitably cause environmental pollution, waste resources, and land occupation. The main mineral components in SS are CaO, Fe₂O₃, SiO₂, MgO, Al₂O₃, and RO, all of which are highly crystalline phases. The main chemical components in SS are CaO, Fe₂O₃, SiO₂, MgO, Al₂O₃, MnO, and P₂O₅. Besides, some SS also contains small amounts of components such as TiO₂ and V₂O₅. SS has attracted widespread attention due to its high content of alkaline substances, high pH value of the slurry, and the coproduction of high-value-added silica gel following desulfurization. If SS is used to replace limestone in wet flue desulfurization, CO₂ emissions will be significantly reduced. In addition, as a byproduct of desulfurization, gyspum has potential as a retarder in the production of Portland cement.

Previous studies have shown that SS or other calcium-based alkaline solid wastes such as fly ash, red mud, and waste concrete can be used for flue gas desulfurization. Liu et al. proposed a method to simultaneously remove SO₂ and NOx from coke oven flue gas using SS slurry. After optimizing the reaction conditions, the removal ratios of SO₂ and NOx were 100% and 83.4%, respectively. Meng et al. proposed a method combining ozone oxidation and (NH₄)₂S₂O₃/SS slurry to simultaneously remove SO₂ and NOx from flue gas. The median diameter of the SS sample after grinding was 74 μm. Under optimal operating conditions, the removal efficiency of SO₂ was close to 100%, and the removal efficiency of NOx was >78.0%. Over-exploitation of natural limestone in the wet flue gas desulfurization process has caused significant ecological damage. To reduce the consumption of natural limestone, Liu et al. used waste concrete particles (WCPs) produced by a waste concrete recycling plant as an alternative desulfurization absorbent to remove SO₂. The results showed that the slurry prepared by dissolving WCP in water was strongly alkaline and rich in Ca²⁺. The WCP slurry effectively removed SO₂ from flue gas, and the desulfurization efficiency reached >98%. The desulfurization capacity of WCP was between 0.44 and 0.73 (g SO₂/g WCP), a SO₂ removal capacity typical of existing calcium-rich desulfurizers. Chen et al. developed a method to simultaneously remove NOx–SO₂–CO₂ using fly ash in supergravity rotating packed bed (RPB). The most important factors influencing mass transfer were investigated, including the high gravity coefficient (β), gas–liquid ratio (GLR), and liquid–solid ratio (LSR). The optimal conditions for simultaneous removal of NOx–SO₂–CO₂ in RPB were β of 233.8, GLR of 69.5, and LSR of 40. Researchers explore ways to improve the desulfurization efficiency, but the extraction and application of the silica gel product have not been reported. The use of SS desulfurization to synergistically extract silica gel is not only of theoretical significance, but, more importantly, it can support the development of value-added SS desulfurization products and the comprehensive utilization of solid waste resources.

Silica gel is a nontoxic and odorless amorphous substance. It is a highly active porous absorbent material prepared by reaction of sodium silicate and sulfuric acid after a series of subsequent treatments. The main component is silicon dioxide, and the molecular formula is mSiO₂·nH₂O. Silica gel has a tetrahedral structure with silicon atoms at the center and oxygen atoms at the apex. The main structure of silica gel is composed of irregular stacks of these tetrahedrons. There are many Si–OH and Si–O–Si bonds on the surface of silica gel. Although there are two lone pairs of electrons provided by oxygen atoms in Si–O–Si, these lone pairs of electrons form a π electron cloud, in which electrons interact with each other and cannot form strong active adsorption sites. In the silicic hydroxyl (Si–OH) groups on the surface, the hydroxyl oxygen atom has a strong electron-donating ability; hence, Si–OH groups are active adsorption sites.

As mentioned above, SS is used instead of limestone for flue gas wet desulfurization, which can reduce the mining of limestone, reduce CO₂ emissions, and also produce high-value-added silica gel. However, there are no relevant reports on coproduction of silica gel following SS desulfurization, and the desulfurization mechanism remains unclear. In this study, SS was used to remove SO₂ and coproduce silica gel and the desulfurization mechanism was explored. The sulfur fixation rate of SS was calculated and compared with those of existing calcium-rich desulfurizers. Extracted silica gel was characterized and applied to the adsorption of methylene blue. The yield of silica gel was calculated, and pore structure parameters were compared with those of commercial silica gel.

### Table 1. Chemical Composition of the SS

| oxide       | CaO     | Fe₂O₃   | SiO₂    | MgO     | MnO     | P₂O₅    | Al₂O₃   | V₂O₅   |
|-------------|---------|---------|---------|---------|---------|---------|---------|--------|
| content (wt %) |         |         |         |         |         |         |         |        |
| CaO         | 37.10   | 20.60   | 15.80   | 7.06    | 3.53    | 3.44    | 2.20    | 0.88   |
| CO₂         | 37.10   | 20.60   | 15.80   | 7.06    | 3.53    | 3.44    | 2.20    | 0.88   |

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

Steel slag (SS) was a basic oxygen furnace slag (BOF) collected from Sichuan Dazhou Iron and Steel Plant (China). It was pulverized into ultrafine powder by a supersonic steam-jet smasher. The steam temperature was 270 °C, and the steam pressure was 1.2 MPa. The D₁₀₀ of SS was 3.15 μm. The ultrafine SS powder was dried and then bagged for later use. In the flue gas wet desulfurization process, air needs to be blown in through a Roots blower outside the desulfurization tower to oxidize the desulfurization product calcium sulfate to calcium sulfate. Therefore, the gas used in the experiment was controlled by dual cylinders, the volume ratio of O₂ and N₂ was 5%:95%, the volume ratio of O₂ and N₂ was 25%:75%, and the ratio of the intake flow rate of the dual cylinders was 1:1. After mixing through the gas distribution device, the mixed gas was passed into the reactor, and the inlet flow rate was 0.8 mL/min. The dialysis bag trapped molecules with a molecular weight of 8000–14 000. Methylene blue was an analytically pure reagent and used directly without purification. Deionized (DI) water was provided by the lab. The chemical components and particle sizes of SS are listed in Tables 1 and 2, respectively.

#### 2.2. Methods

##### 2.2.1. Using SS to Remove SO₂

First, 100.00 mL of DI water was placed in a three-necked flask on a thermostatic heating magnetic stirrer. At a solid/liquid ratio of 1:10, 10.0000 g of SS was added to the beaker and stirred at a steady rate, and a pH meter was used to record changes in pH.
online. After the pH value was stable, a mixed gas of SO₂ and O₂ at a flow ratio of 1:1 was introduced at a flow rate of 0.8 mL/min, and changes in slurry pH were monitored online to obtain a curve of slurry pH vs time. When the pH value stabilized, ventilation was stopped and the reaction was finished. The resulting slurry was vacuum-filtered to yield a solid product and a filtrate. The solid product was placed in an oven at 105 °C, dried to a constant weight, and bagged and sealed for testing. The filtrate was put in a dialysis bag and placed in water for dialysis to extract silica gel. Each experiment was performed three times, and the results are expressed as mean ± standard deviation. The experimental setup is shown in Figure 1.

2.2.2. Silica Gel Extraction Process. The dialysis bag containing the desulfurized filtrate was soaked in a beaker containing DI water, and the water was continuously changed. Before changing the water, a conductivity meter was used to measure the conductivity of the DI water and the DI water in the dialysis bag. When the two values were similar, dialysis was considered complete. Next, the solution in the dialysis bag was divided into two parts; one part was poured into a beaker to allow most of the water to escape via steam and then placed in an oven for drying; the other part was frozen and placed in a freeze dryer. Silica gel particles obtained by both treatment methods were sealed in bags for testing. A group of the materials after the desulfurization reaction was characterized by a Fourier transform infrared spectrometer (PerkinElmer 1730). The FT-IR spectra of all samples were collected over a wavenumber from 400 to 4000 cm⁻¹ with the KBr pellet method. The sulfur contents in the raw materials and desulfurization products were determined by thermal gravimetric analysis (Pyris 1, PerkinElmer) with an Al₂O₃ crucible. The N₂ pressure was 0.2−0.3 MPa, and the purge gas of N₂ was at 0.3 MPa. The heating rate was 10 °C/min. The heating temperature was from 50 to 850 °C. The functional groups of the materials after the desulfurization reaction was characterized by a Fourier transform infrared spectrometer (PerkinElmer 1730). The FT-IR spectra of all samples were collected over a wavenumber from 400 to 4000 cm⁻¹ with the KBr pellet method. The sulfur contents in the raw materials and desulfurization products were determined by an automatic sulfur analyzer (Sundy, China). The absorbance was measured by an ultraviolet—visible spectrophotometer (UV-2600i, Shimadzu, Japan). The specific surface areas and pore structure parameters were obtained by measuring the N₂ adsorption isotherm of silicone at liquid nitrogen temperature on a physical sorbent (ASAP2460) using the monolayer adsorption and capillary condensation theory. All samples were preprocessed before characterization, and samples were degassed for 1 and 12 h at 90 and 120 °C, respectively.

3. RESULTS AND DISCUSSION

3.1. pH Changes during Desulfurization. Various reactions occurred during the desulfurization process as follows Figure 3

| size | SS |
|------|----|
| D₁₀₀ | 1.22 |
| D₅₀  | 3.15 |
| D₁₀  | 6.27 |

Table 2. Particle Size Distribution of SS (μm)

using a generator voltage of 50 kV and a tube current of 40 mA. The diameter of the irradiation hole was 20 mm. Particle sizes of SS were determined by a laser particle size analyzer (Mastersizer 3000, Malvern, Germany). The mineralogical compositions of SS and desulfurization products were analyzed by an X-ray diffractometer (D2-Phaser, Bruker, Germany) with a Cu Kα source at 40 kV and 40 mA. The divergence slit was fixed at 0.38 mm, and a divergence angle of 10−80° was scanned at a rate of 0.02° s⁻¹. The morphologies of SS and the desulfurization products were determined with a scanning electron micrograph coupled with an energy-dispersive X-ray spectrometer (SEM-EDS, JSM-IT500HR, Japan). The sample was mounted on the copper sample holder with conducting resin, and the sample surface was coated by gold spraying. The thermal weight loss of desulfurization products was measured by thermal gravimetric analysis (Pyris 1, PerkinElmer) with an Al₂O₃ crucible. The N₂ pressure was 0.2−0.3 MPa, and the purge gas of N₂ was at 0.3 MPa. The heating rate was 10 °C/min. The heating temperature was from 50 to 850 °C. The functional groups of the materials after the desulfurization reaction was characterized by a Fourier transform infrared spectrometer (PerkinElmer 1730). The FT-IR spectra of all samples were collected over a wavenumber from 400 to 4000 cm⁻¹ with the KBr pellet method. The sulfur contents in the raw materials and desulfurization products were determined by an automatic sulfur analyzer (Sundy, China). The absorbance was measured by an ultraviolet—visible spectrophotometer (UV-2600i, Shimadzu, Japan). The specific surface areas and pore structure parameters were obtained by measuring the N₂ adsorption isotherm of silicone at liquid nitrogen temperature on a physical sorbent (ASAP2460) using the monolayer adsorption and capillary condensation theory. All samples were preprocessed before characterization, and samples were degassed for 1 and 12 h at 90 and 120 °C, respectively.

3. RESULTS AND DISCUSSION

3.1. pH Changes during Desulfurization. Various reactions occurred during the desulfurization process as follows Figure 3

Figure 1. Schematic diagram of the experimental apparatus. Note: (1) SO₂ + N₂ cylinder; (2) O₂ + N₂ cylinder; (3) gas flow meter; (4) gas mixing tank; (5) magnetic stirring; (6) reaction glass container; (7) condenser; (8) pH meter; (9) NaOH solution.
introduction of SO$_2$ reduced the amount of reactive alkaline substances in the slurry; hence, the reaction slowed down. When the reaction time reached 1800 s, the pH was 3.48, and it did not change as the reaction time was extended. At this time, the desulfurization reaction had essentially finished. In stage e, to verify whether the desulfurization reaction was complete, the introduction of SO$_2$ was stopped at 1800 s, and the pH value of the slurry tended to increase and stabilized at around 7.10 with no further change. This showed that the alkaline substances in the slurry had reacted fully, and the desulfurization reaction was over.

### 3.2. Sulfur Fixation Ratio
The sulfur fixation ratio of SS was defined as the mass of SO$_2$ removed by SS per unit mass, calculated using eq 10:

$\zeta = \frac{W_{\text{products,SO}_2} \times 100}{W_{\text{SS}}} = \frac{W_{\text{products,SO}_2} - W_{\text{raw material,SO}_2}}{1 - (W_{\text{products,SO}_2} - W_{\text{raw material,SO}_2})} \times 100\%$  

(10)

where $\zeta$ represents the desulfurization efficiency, $W_{\text{products,SO}_2}$ represents the percentage of SO$_2$ in the products, $W_{\text{SS}}$ represents the percentage of SS in the product, and $W_{\text{raw material,SO}_2}$ represents the percentage of SO$_2$ in the SS raw material.

Data measured by the sulfur analyzer were entered into eq 10, and the relevant parameters and calculation results are shown in Table 3. SS with a median diameter of 3.15 $\mu$m was used to remove SO$_2$; the sulfur fixation ratio was 40.67%; this means that 1 ton of SS can fix 406.7 kg of SO$_2$, a SO$_2$ removal efficiency typical of existing calcium-rich desulfurizers. In other words, if limestone desulfurization was replaced with SS of equal
3.3. Yield of Silica Gel. The yield of coproduced silica gel after desulfurization was defined as the mass of silica gel

desulfurization ratio, CO₂ emission can be reduced by 279.6 kg and limestone can be reduced by 635.5 kg.

Table 3. Desulfurization Efficiency Parameters of SS

|           | sulfur content was calculated as SO₃ (%) | sulfur content was calculated as SO₂ (%) | desulfurization efficiency (%) |
|-----------|------------------------------------------|------------------------------------------|---------------------------------|
| SS        | 1.12 0.95 1.08 1.05                      | 0.84                                     | 40.67                           |
| desulfurization products | 38.28 36.52 36.65 37.19                  | 29.75                                    |                                 |

Figure 4. FT-IR spectra of (a) liquid products of desulfurization and (b) solid products of desulfurization.

Figure 5. XRD patterns of (a) SS raw material and (b) solid products of desulfurization.
extracted per unit mass of SS after the desulfurization reaction. The yield of silica gel was calculated according to eq 11

\[
\eta = \frac{m_{\text{silica gel}}}{m_{\text{SS}}} \tag{11}
\]

where \(\eta\) represents the yield of silica gel, \(m_{\text{silica gel}}\) (g) represents the mass of silica gel generated after the desulfurization reaction, and \(m_{\text{SS}}\) (g) represents the mass of SS used in the desulfurization reaction. After weighing and calculation, the yield of silica gel in this study was 5.1%. Thus, \(\sim 51\) kg of silica gel could be extracted per ton of SS after desulfurization. At present, the price of industrial-grade ordinary silica gel on the market is \(\sim 32,000\) yuan per ton, and then the value of the byproduct of desulfurization of SS is \(\sim 1600\) yuan per ton, making it of significant economic value.

### 3.4. Analysis and Characterization of Desulfurization Solid Products

#### 3.4.1. FT-IR Analysis

Figure 4 shows the FT-IR spectra of the solid-phase product and silica gel after desulfurization. The absorption peaks observed at 3435 and 1639 cm\(^{-1}\) can be attributed to the stretching vibration band of \(-\text{OH}\) in silica gel (Figure 4a). There was a strong absorption peak at 1087 cm\(^{-1}\), which was assigned to the antisymmetric vibration absorption peak of the Si–O–Si bond in silica gel. The adsorption peak at 799 cm\(^{-1}\) was related to the symmetric vibration absorption peak of Si–O–Si.\(^{16-18}\) It can be seen from Figure 4 that there was no obvious impurity peak in the FT-IR spectra of the prepared silica gel; hence, the prepared silica gel was of high purity. The stretching vibration absorption of O–H occurred at 3406 cm\(^{-1}\), and the deformation vibration of H–O–H occurred at 1620 cm\(^{-1}\) for crystal water in calcium sulfate (Figure 4b). The presence of the adsorption band at 1147 cm\(^{-1}\) was related to the in-plane bending vibration of SO\(_4^{2-}\), and the absorption bands at 652 and 602 cm\(^{-1}\) were due to the discrete peak of the out-of-plane bending vibration.\(^{19}\) The absorption bands at 990 cm\(^{-1}\) corresponded to the vibration absorption of Si–O–Si, and the absorption bands at 953 cm\(^{-1}\) corresponded to the vibration absorption of Si–OH. This indicated that part of the silica gel generated after the desulfurization reaction also existed in the solid-phase products. The absorption bands observed at 1423 cm\(^{-1}\) can be attributed to the antisymmetric stretching vibration peak of the C–O group of CaCO\(_3\) in raw SS.\(^{20-22}\)

#### 3.4.2. XRD Analysis

The XRD results for SS raw materials and desulfurization products are shown in Figure 5. Strong diffraction peaks for Ca(OH)\(_2\) and CaCO\(_3\) were detected in SS samples. Obvious diffraction peaks for dicalcium silicate (C\(_2\)S) and tricalcium silicate (C\(_3\)S) and relatively weak diffraction peaks for Ca\(_2\)Fe\(_2\)O\(_5\) and the RO phase were also detected in SS. The diffraction peaks at 2θ of 14.6, 20.8, 25.5, and 29.8° in the desulfurization product were from CaSO\(_4\)·2H\(_2\)O, and the diffraction peaks at 31.8, 34.0, and 53.9° were from CaSO\(_4\)·0.5H\(_2\)O. The diffraction peaks at 15.9, 18.2, 23.4, 28.1, and 36.4° were from CaSO\(_3\)·0.5H\(_2\)O, among which CaSO\(_3\)·0.5H\(_2\)O had the largest number of diffraction peaks and peaks with the strongest intensity. From the above analysis, it can be seen that after the desulfurization reaction, Ca(OH)\(_2\), CaCO\(_3\), C\(_2\)S, and C\(_3\)S in SS participated in the reaction and generated CaSO\(_4\)·2H\(_2\)O, CaSO\(_4\)·0.5H\(_2\)O, and CaSO\(_3\)·0.5H\(_2\)O.
3.4.3. SEM Analysis. Comparison with raw SS revealed obvious block-shaped crystals in the desulfurization product (Figure 6). Combined with the EDS analysis results, we can conclude that these crystals were CaSO₄. CaSO₄ was tightly wrapped on the surface of SS, so that the active sites of SS that participated in the desulfurization reaction were reduced, which will inevitably hinder subsequent desulfurization reactions, which may be the main reason for reducing the sulfur fixation ratio of SS.

3.4.4. TG−DTG Analysis. To study the thermal weight loss characteristics of the solid-phase products of desulfurization, solid-phase products were analyzed by TG−DTG, and the results are shown in Figure 7. Solid-phase products displayed four obvious weight loss stages. In the first stage, the temperature range of weight loss was 35.5−100.2 °C, the peak temperature of weight loss was 93.9 °C, and the weight loss ratio was 3.5%. This was due to the loss of free water in solid products. In the second stage, the temperature range of weight loss was 100.2−252.6 °C, the peak temperature of weight loss was 110.1 °C, and the weight loss ratio was 4.0%. This was due to the loss of crystal water from solid products. In the third stage, the temperature range of weight loss was 329.5−433.7 °C, the peak temperature of weight loss was 432.1 °C. In the fourth stage, the temperature range of weight loss was 433.7−1000 °C, the peak temperature of weight loss was 491.8 °C, and the weight loss ratio was 10.5%

Figure 7. TG−DTG curves of solid products of desulfurization.

Figure 8. SEM-EDS images of the liquid product evaporated residues (a) and freeze-dried products (b).
temperature of weight loss was 391.2 °C, and the weight loss ratio was 2.8%. This was due to the thermal decomposition of Ca(OH)₂ in raw SS that was not involved in the desulfurization reaction.23,24 In the fourth stage, the temperature range of weight loss was 627.3−747.6 °C, the peak temperature of weight loss was 721.5 °C, and the weight loss ratio was 1.2%. This was due to the thermal decomposition of CaCO₃ in SS that did not participate in the desulfurization reaction.25−28 From the above analysis, we can conclude that part of Ca(OH)₂ and CaCO₃ did not participate in the desulfurization reaction in the system. This may be because the desulfurization product particles covered the surface of SS particles and prevented further progress of the reaction; hence, it is essential to reduce the SS particle diameter using a supersonic steam-jet smasher to expose more reactive active sites. The weight loss ratio of the whole process was 11.5%.

3.5. Analysis and Characterization of Silica Gel.

3.5.1. SEM Analysis. The liquid-phase product was heated, evaporated to dryness, freeze-dried, and then analyzed by SEM-EDS, and the results are shown in Figure 8. The surface of the products obtained by direct evaporation is dense, and a large number of particles are randomly accumulated on the solid surface (Figure 8a). Combined with EDS analysis, we can conclude that these particles were SiO₂ and that silica gel (mSiO₂·nH₂O) was formed following desulfurization. A large number of random accumulations of particulates on the surface of the freeze-dried sample are evident (Figure 8b). Also, EDS analysis showed that this was an amorphous SiO₂ particulate. The difference is that pores appeared on the sample surface after freeze-drying. This is because silica gel is a colloidal substance that swells after absorbing water and shrinks after dehydration;29 hence, the pores remain after freeze-drying. This shows that silica gel has the potential for adsorption.

3.5.2. XRD Analysis. The results of XRD analysis of the silica gel sample are shown in Figure 9a. There was a significant used peak in the XRD spectrum, which was attributed to the amorphous SiO₂ peak cluster,30,31 indicating that the prepared silica gel sample consisted of amorphous SiO₂. The silica gel had an amorphous structure. No other sharp crystal diffraction peaks were observed in the XRD spectrum. This showed that the purity of the prepared silica gel was relatively high. As shown in Figure 9b, the laser lamp passed cleanly through the liquid-phase product; hence, a Tindal effect occurred, which can infer the presence of colloids in the desulfurization product. Together with the results discussed above, this proved that the desulfurization product was silica gel.

![Figure 9. XRD analysis of silica gel (a) and Tyndall phenomenon (b).](image)

![Figure 10. Adsorption–desorption isotherms of N₂ (a) and pore-size distribution of silica gel (b).](image)
3.5.3. BET Analysis. According to IUPAC classification, the N₂ adsorption and desorption isotherms of silica gel were similar to type IV isotherms (Figure 10a). In the area of P/P₀ < 0.6, the curve was convexed upward, similar to the type II isotherm. In the region of P/P₀ > 0.6, the adsorption and desorption isotherms showed a rapid upward trend, which was caused by the capillary condensation of the adsorbate. When all pores had coalesced, adsorption only occurred on the outer surface, but because the outer surface was much smaller than the inner surface, the curve was flat. Close to a relative pressure of 1, when adsorption occurred at large pores, the curve raised. The adsorption and desorption isotherms did not overlap, and the desorption isotherm was located above the adsorption isotherm; hence, a desorption hysteresis (a hysteresis loop) appeared (Figure 10a). The reason for this was that capillary condensation occurred in this region, causing a hysteresis, which was related to the shape of the pore and its size. The arrest loop belonged to type H₃; hence, there was no obvious saturation adsorption platform in the isotherm due to the irregularity of the sample pore structure. As shown in Figure 10b, the aperture distribution of silica gel was mainly an inter pore of 2–24 nm.

The pore structure parameters of silica gel prepared in this research and commercial fine-pored silica gel and B-type silica gel were compared. The pore structure of B-type silica gel was between coarse-pored and fine-pored silica gel (Table 4). The pore structure parameters of the silica gel prepared in this research were close to those of commercial B-type silica gel, but the specific surface area was slightly smaller. This may be because the prepared silica gel was not been activated at high temperatures.

3.5.4. TG–DTG Analysis. To investigate the thermal weight loss properties of silica gel, we performed a TG–DTG analysis of the obtained products, and the results are shown in Figure 11. Silica gel displayed a significant weight loss in the range of 19.7–109.6 and 109.6–194.6 °C, with weight loss ratios of 13.1 and 4.6% and weight loss peak temperatures of 56.4 and 122.5 °C, respectively. This is due to the dehydration of silica gel. Within a temperature range of 123–1000 °C, the TG curve showed a significant downward trend with a weight loss ratio of 10.7% and no significant peak temperature on the DTG curve. This suggested that silica gel dehydration also occurred in this temperature range. This is because with an increase of temperature, the silanol group on the surface of silica gel began to dehydrate and formed the −Si−O−Si bond.

3.6. Desulfurization Mechanism. Based on the above results, we concluded that the process of using SS to remove SO₂ involves three stages. In the first stage, when the flue gas enters the SS slurry, SO₂ quickly dissolves into the water to generate SO₃²⁻, HSO₃⁻, and H₂SO₃. SO₃²⁻ is oxidized to SO₄²⁻ under the action of dissolved oxygen. The specific process can be described as follows: (1) SO₂ and O₂ diffuse from the gas phase to the gas–liquid interface; (2) SO₂ and O₂ dissolve in the liquid phase according to Henry’s law; (3) SO₂ is hydrated with water to form sulfuric acid, and it then ionizes to produce H⁺, SO₃²⁻, and HSO₃⁻; (4) H⁺, SO₃²⁻, HSO₃⁻, and O₂ dissolve in the liquid phase; and (5) SO₃²⁻ and HSO₃⁻ are oxidized to SO₄²⁻ by dissolved oxygen in the liquid phase. In the second stage, free CaO in the SS particles is hydrolyzed in the slurry to generate Ca(OH)₂, which releases a large amount of Ca²⁺ in the slurry. In an environment where SO₂ is dissolved in the slurry to generate acidic conditions, C₃S, C₃S, and Ca₂Fe₂O₅ also release Ca²⁺. The content of Fe in the SS used in this study was 20.6% as Fe₂O₃, the second-most abundant element. According to previous reports, Fe promotes the desulfurization reaction, which is another advantage of SS replacing limestone in flue gas wet desulfurization. In the third stage, Ca²⁺ reacts with SO₄²⁻ and SO₃²⁻ to generate block-shaped CaSO₄·2H₂O, CaSO₄·0.5H₂O, and CaSO₄·H₂O, which adhere to the surface of SS particles. The generated silica gel is a colloidal substance with a particle size <100 nm, which can enter the filtrate through the pores of the filter paper. The mechanism of removing SO₂ by SS is shown in Figure 12.

3.7. Optimization of Reaction Conditions for Adsorption of Methylene Blue on Silica Gel. 3.7.1. Influence of

| Table 4. Pore Structural Parameters of Silica Gel |
|-------------|-------|-------|-------|
|             | Sₐₘ (m²·g⁻¹) | Sₐₜ (m²·g⁻¹) | dₐ (nm) |
| this study   | 334.6 | 20.9  | 0.555 | 6.64 |
| commercial fine-pored silica gel | 650–800 | 0.35–0.40 | 2.0–3.0 |
| commercial B-type silica gel | 450–650 | 0.60–0.85 | 4.5–7.0 |

Figure 11. TG–DTG curves of silica gel.
Figure 12. Schematic diagram of the mechanism of removing SO\textsubscript{2} by SS.

Figure 13. Effects of (a) silica gel dosage, (b) initial concentration of methylene blue, and (c) pH value on removal ratio.
Silica Gel Dosage on Removal Ratio. At a methylene blue concentration of 0.012 mg/mL, room temperature, and a reaction time of 30 min, the influence of the dosage of silica gel on the removal ratio of methylene blue was investigated, and the results are shown in Figure 13a.

At silica gel dosages of 20, 25, 30, 35 and 40 mg, the removal ratios of methylene blue were 97.4, 97.8, 98.4, 96.7, and 97.2%, respectively. The dosage of silica gel had little effect on the removal ratio of methylene blue, and the optimal dosage was 30 mg. When the dosage was <30 mg, the adsorbent dosage may be too low; hence, the removal ratio was low; when the dosage was >30 mg, because silica gel is a colloidal substance, it swells after absorbing water; hence, it will be completely suspended in the upper phase following centrifugation, resulting in high absorbance and low removal ratio.

3.7.3. Effect of pH on Removal Ratio. At a silica gel dosage of 30 mg/mL, room temperature, and a reaction time was 30 min, the effect of methylene blue pH value on the removal ratio was investigated, and the results are shown in Figure 13c.

When the pH levels of methylene blue were 2.00, 4.00, 6.00, 8.00 and 10.00, the removal ratios of methylene blue were 95.8, 98.5, 98.3, 98.5, and 98.4%, respectively. The removal ratio of methylene blue was not changed significantly, except for the low removal ratio at pH 2.00. Thus, strong acidic conditions were not conducive to the adsorption of methylene blue. This may be because under acidic conditions, H⁺ in solution may compete with methylene blue cations for adsorption, and the adsorbent surface would become positively charged, which would generate electrostatic repulsion of methylene blue cations, resulting in low adsorption capacity and low removal ratio. When the pH is increased, hydrogen bonding between the hydroxyl groups and methylene blue cations on the surface of silica gel is strengthened, the surface of the adsorbent is negatively charged, and electrostatic attraction between the surface of the adsorbent and methylene blue cations will increase the adsorption capacity and the removal ratio.

3.8. Mechanism of Silica Gel Adsorption of Methylene Blue. The mechanism of the adsorption of methylene blue on the silica gel byproduct of SS desulfurization was considered. The adsorption capacity of a solid adsorbent depends not only on the specific surface area and pore structure but also on the surface characteristics (i.e., the functional groups on the surface of the adsorbent). There are six mechanisms for describing adsorption on a solid surface: electrostatic interaction, ion exchange, ion—dipole interaction, surface metal cation coordination, and hydrophobic interaction. The main force between silica gel and methylene blue is electrostatic attraction. The Si—OH groups on the surface of silica gel ionize to give generate H⁺ and [SiO]⁻, which combines with the cationic dye MB⁺ through the attraction between positive and negative charges. Under acidic conditions, the amount of H⁺ in the solution is large, and this cation may compete with MB⁺ for adsorption on the surface of silica gel, which will reduce the adsorption rate of MB⁺. However, when the pH of the solution is increased, the reaction between OH⁻ and H⁺ will increase the number of [SiO]⁻ groups on the surface of the silica gel, which will inevitably increase the MB⁺ adsorption ratio. This is consistent with the results described above. In addition, hydrogen bonds form between the H atoms of the Si—OH groups on the surface of the silica gel and the N atoms of the methylene blue molecules. Thus, both electrostatic attraction and hydrogen bonding may occur between silica gel and methylene blue molecules. This conclusion is consistent with previous research. A schematic diagram of the adsorption process is shown in Figure 14.
4. CONCLUSIONS
SS has a high Ca content, and the slurry is strongly alkaline; hence, it can be used for the removal of SO2 and can replace natural ore limestone in the limestone–gypsum desulfurization process of thermal power plants, thereby avoiding discharge of CO2 from limestone during the desulfurization process. This is compatible with the “use waste to treat waste” concept, and it can also produce high-value-added silica gel as a byproduct. Our study mainly examined the sulfur fixation ratio of SS for removing SO2, the yield of silica gel, and the optimal conditions for silica gel adsorption of methylene blue. The main conclusions are as follows:

(1) At a solid–liquid ratio of 1:10, room temperature, and a constant stirring speed, SS with a D_{50} of 3.15 μm was used to remove SO2. The results showed that 1 ton of SS can remove 406.7 kg of SO2 and yield 51.0 kg of silica gel. In other words, 1 ton of SS can remove 406.7 kg of SO2, reduce CO2 emissions by 279.6 kg, and save 635.5 kg of limestone.

(2) FT-IR, XRD, SEM-EDS, and TG–DTG showed that the main products following desulfurization were CaSO4·2H2O, CaSO4·0.5H2O, CaSO4·0.5H2O, and silica gel.

(3) The optimal methylene blue adsorption conditions are a silica gel dosage of 30 mg, a temperature of 20 °C, a pH of 6.00, a stirring time of 0.5 h, and a methylene blue concentration of 0.02 mg/mL. The removal ratio of methylene blue adsorbed by silica gel was 98.4%.

(4) Two forces (electrostatic attraction and hydrogen bonding) appear to occur between silica gel and methylene blue molecules, but the most important force is electrostatic attraction. Thus, Si–OH groups on the surface of the silica gel ionize to generate H+ and [SiO]−, which combines with the cationic dye MB+ through the adsorption of positive and negative charges. In addition, hydrogen bonds are formed between H atoms of Si–OH groups on the surface of the silica gel and N atoms of the methylene blue molecules.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Major Scientific and Technological Innovation Project of Shandong Province (No. 2019JZZY020306) and China’s National Key Research and Development Program (2020YFB0606204).

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