Carbon consumption and adsorption-regeneration of H$_2$S on activated carbon for coke oven flue gas purification

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Abstract
Carbon consumption of activated carbon varies with sulfur-containing products. In this work, differential thermogravimetric (DTG), electron paramagnetic resonance (ESR), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD) were used to reveal the adsorption-regeneration process of H$_2$S and the effect of adsorption products on carbon consumption. The results show that H$_2$S reacts with the C=C bond to form the C-S bond as an intermediate state, followed by the formation of elemental sulfur. It directly sublimes at approximately 380 °C, about 30 °C higher than the decomposition temperature of H$_2$SO$_4$. In the thermal regeneration process, the elemental sulfur in the form of monoclinic sulfur (S$_8$) first breaks into infinitely long chain molecules (S$_\infty$) and then into small molecules, finally into sulfur vapor. The desorption of elemental sulfur consumes less oxygen and carbon functional groups, reducing the chemical carbon consumption by 59.8% than H$_2$SO$_4$; moreover, the compressive strength reduces less due to its slight effect on the disordered graphitic structure. H$_2$S also reacts with the C=O bond to form H$_2$SO$_3$ or H$_2$SO$_4$. The desorption of H$_2$SO$_3$ does not require carbon consumption. The decomposition of H$_2$SO$_4$ needs to react with the C=C bond to release SO$_2$, CO$_2$, and CO, and the compressive strength of activated carbon significantly decreases. The carbon consumption originates from two aspects; the one from the regeneration of sulfur-containing products is more than twice the other one from the decomposition of oxygen-containing functional groups.

Keywords Activated carbon · Hydrogen sulfide · Elemental sulfur · Chemical carbon consumption · Physical carbon abrasion

Introduction
Due to the leakage of coke oven gas from the furnace wall, coke oven flue gas contains approximately 130–165 ppm H$_2$S in addition to 50 ppm SO$_2$, and this issue must then be ameliorated by oxidation (Vinod and Tawfik 2013). Activated carbon treatment of H$_2$S and SO$_2$ in flue gas is an environmentally friendly and effective purification technology (Braghiroli et al. 2019; Grzyb et al. 2009; Liu et al. 2003; Nguyen-Thanh and Bandosz 2005; Rubio and Izquierdo 2010), which has many advantages, such as removal of multipollutants and no secondary pollution. However, the operation cost per year is relatively high which is attributed to the supplement of activated carbon. Therefore, the carbon consumption should be reduced for sustainable development and cleaner production.

Carbon consumption of activated carbon purification technology is obviously different under various industrial flue gas. For a long-term operation, it is found that the carbon consumption in sintering flue gas purification is 1.15–1.2 times higher than that in coke oven flue gas purification. Both flue gas has a similar NO concentration of about 300–400 ppm and total sulfur concentration of about 200–300 ppm. While sintering flue gas only contains SO$_2$, coke oven flue gas includes H$_2$S as well as SO$_2$. That is, the presence of H$_2$S may decrease the carbon consumption. At present, there is little research on the effects of H$_2$S on carbon consumption of activated carbon for flue gas purification.

Both H$_2$S and SO$_2$ in coke oven flue gas can cause sulfur species deposition on the activated carbon, which is usually treated with thermal regeneration to recover the reaction
activity (Li et al. 2019a; Qi et al. 2014; Silas et al. 2018). In the adsorption process, \( \text{SO}_2 \) combines with basic functional groups to generate \( \text{H}_2\text{SO}_4 \) (Guo et al. 2013; Karatepe et al. 2008; Xu et al. 2018). \( \text{H}_2\text{S} \) can be oxidized to sulfur, \( \text{H}_2\text{SO}_3 \), and \( \text{H}_2\text{SO}_4 \), which depend on the activated carbon surface properties and the atmosphere. \( \text{H}_2\text{S} \) associates with the oxygen functional groups on the activated carbon surface, producing \( \text{H}_2\text{SO}_4 \) and elemental sulfur. With \( \text{O}_2 \) in the atmosphere, \( \text{H}_2\text{S} \) can be oxidized to elemental sulfur and then to produce gaseous \( \text{SO}_2 \) (Li et al. 2019a). In the thermal regeneration process, \( \text{H}_2\text{SO}_4 \) can react with activated carbon to release \( \text{SO}_2 \) and simultaneously produce CO and \( \text{CO}_2 \), which are the main sources of chemical carbon consumption (Li et al. 2019b). \( \text{H}_2\text{SO}_4 \) decomposes at a lower temperature, so its chemical carbon consumption is essentially negligible (Kim et al. 2019). Currently, the transformation of elemental sulfur in the regeneration process and its chemical carbon consumption are rarely studied.

Carbon consumption consists of chemical carbon consumption and physical carbon abrasion. The chemical carbon consumption is from the regeneration of the sulfur-containing components. The physical carbon abrasion is related to the mechanical strength of the activated carbon as well as the moving speed of the activated carbon in the reactor. Regeneration also alters the lattice structure of the activated carbon and then affects its mechanical strength. To date, few studies have focused on this issue.

The proportion of operation cost is calculated based on the coke oven flue gas purification project from HBIS Group Hansteel Company in Hebei province, China, as follows: electricity charges 27%, \( \text{N}_2 \) charges 22%, activated carbon charges 20%, ammonia charges 7%, steam charges 6%, blast furnace gas charges 6%, and other charges 12%. The consumption of activated carbon is relatively high, which can be further optimized and reduced. Therefore, this work focuses on carbon consumption in the process of flue gas purification. Firstly, the deposition products of three typical sulfur-containing components were prepared on activated carbon in various adsorption atmospheres, and then, the regeneration process was studied to elucidate the effect of sulfur-containing substances on the physical structure and chemical characteristics of activated carbon. The sources of physical carbon abrasion and chemical carbon consumption were studied, and the strategy of reducing carbon consumption was put forward.

**Material and methods**

**Activated carbon preparation**

The anthracite-based activated carbon (AC) is from Shanxi province. The material in the lab was pulverized, sieved to 20–60 mesh (0.25–0.85 mm), rinsed with deionized water, filtered, and dried in a drying oven at 110 °C for 20 h; the activated carbon thus treated was marked as fresh AC. The fresh AC sample was pretreated in a fixed bed reactor with a diameter of 30 mm, with 1.50 ± 0.01 g sample charged, and then reacted with the mixture gas at a gas hourly space velocity of 5700 h\(^{-1}\) at 150 °C for 300 min. Four samples named blank sample and AC\(_1\)–AC\(_3\) were obtained in different gas: blank sample, \( \text{N}_2; \text{AC}_1, 50 \text{ppm} \text{SO}_2 \) and 150 ppm \( \text{H}_2\text{S}; \text{AC}_2, 200 \text{ppm} \text{SO}_2; \) and \( \text{AC}_3, 200 \text{ppm} \text{SO}_2 \) and 5% \( \text{O}_2 \), with the balance \( \text{N}_2 \). The total molar contents of the sulfur substances, the adsorption time, and the activated carbon used in the experiment were the same for the AC\(_1\)–AC\(_3\) samples.

**Experimental conditions**

The thermal regeneration process on the activated carbon samples was investigated in the abovementioned fixed bed reactor. The regeneration process was carried out in \( \text{N}_2 \), and the gas flow rate was 180 ± 5 mL/min at a heating rate of 5 °C/min from 150 °C to the final temperature of 450 °C. The regenerated activated carbon was labeled as AC-re.

The outlet concentration of the gas component was tested online by a Fourier transform infrared (FTIR) spectrometer (Tensor 27, Bruker, Germany). The integral area of the thermal regeneration curves could be used to calculate the CO and \( \text{CO}_2 \) contents with a minimum standard deviation of approximately 2%. And the same calculation method was also used for the temperature programmed desorption (TPD) curves obtained at a heating rate of 5 °C/min from 150 °C to 900 °C. Chemical carbon consumption referred to the sum of CO and \( \text{CO}_2 \) emitted per gram of activated carbon (mmol/g) during the regeneration.

**Characterization methods**

Elemental analysis was conducted using an Elemental Analyzer (Vario EL, Elementar, Germany). The C, N, H, and S contents were characterized on the dry ash free (daf) basis of the AC samples with a minimum standard deviation of approximately 0.2%, and the O content was calculated by the difference method.

The pore characteristics were tested by an automatic surface area and porosity analyzer (NOVA3200e, Quantachrome, USA) in \( \text{N}_2 \) at -196 °C. The specific surface area \((S_{\text{BET}})\) was calculated by the multipoint Brunauer-Emmett-Teller (BET) equation. The total pore volume \((V_T)\) was determined by the \( \text{N}_2 \) adsorption capacity at \( p/p_0 = 0.95 \). The graphite microcrystalline structure of the AC samples was characterized by a Raman spectrometer (Renishaw inVia plus, Renishaw, UK).

A simultaneous thermogravimetric (TG) analyzer (Labsys Evo, setaram LABSYS, France) was used to test the TG and
differential TG (DTG) curves over the 30–900 °C range at a heating rate of 5 °C/min in N₂. 50 mg analytically pure sulfur and 50 mg activated carbon were packed in a quartz glass tube and heated in air.

The characterization methods of pore structure, graphite structure, X-ray photoelectron spectroscopy (XPS), and in situ diffuse reflectance infrared Fourier transform (DRIFT) spectra were represented in detail elsewhere (Fang et al. 2013; Li et al. 2018).

The electron paramagnetic resonance (ESR) spectra were measured to test the form of elemental sulfur on an X-band spectrometer (EMXplus-9.5/12, Bruker, USA) at room temperature, 150 °C, and 400 °C.

Mechanical strength was measured using a compression strength tester (HNYQ6000, Huatong, China) and a wear resistance tester (MHXT-2D, Tianguan, China), which were customized according to the GB 30202.3-2013 standard. The average value was obtained after three tests with an error of 1% for wear resistance and 3% for compression strength.

Results and discussion

Decomposition mechanism of sulfur products

To determine the differences in the sulfur-containing adsorption products, an elemental analysis of various AC samples was carried out, and the results are shown in Table 1. The sulfur contents of the AC₁–AC₃ samples are basically the same and significantly higher than that of the blank sample due to the strong adsorption capacity of activated carbon for H₂S and SO₂. For AC₁–AC₃ samples, there is no clear difference in the sulfur and oxygen contents with a deviation of 2%. According to the previous study (Li et al. 2019a), the desulfurization efficiency in the three atmospheres used in the work can reach approximately 95% so that the sulfur contents of the three products are basically the same.

Figure 1 shows the proportions of the elemental sulfur, SO₃²⁻, and SO₄²⁻ calculated from the data in Fig. S1. SO₄²⁻ and elemental sulfur (Liu et al. 2015; Menezes et al. 2018; Qiu et al. 2019) constitute the majority of sulfur products on the activated carbon surface for the four samples. The proportion of elemental sulfur in AC₁ is 65.8%, indicating that the oxidation products of H₂S are mostly elemental sulfur. AC₂ contains approximately 20.8% H₂SO₃, because H₂SO₃ can be formed by the reaction of SO₂ and H₂O in the atmosphere without O₂. However, due to the oxidation of oxygen-containing functional groups on the AC surface, H₂SO₃ will be oxidized to H₂SO₄ (Guo et al. 2013). The SO₄²⁻ content in AC₃ is greater than 60%, because SO₂ is adsorbed at the active site first and then is easily oxidized to H₂SO₄ in the presence of O₂.

According to the analysis of the elemental content and XPS spectra, the total sulfur content is basically the same for AC₁–AC₃, and the difference lies in the forms of sulfur-containing products. The elemental sulfur accounts for the majority of the sulfur species in AC₁, while AC₂ contains 20.8% H₂SO₃, and the main sulfur product in AC₃ is H₂SO₄. The existence form of sulfur-containing products is determined by the adsorption atmosphere.

The XPS results of carbon and oxygen functional groups are shown in Tables S1 and S2. As shown in Fig. 2a, compared with the blank sample, the amount of C=C and C=O bonds of AC₁ clearly decrease, while the C-S bond increases. According to previous studies (Silas et al. 2018), in the process of H₂S oxidation, the C=C bond and C=O bond have been broken by H₂S, and then, the C-S bond and S-O bond are generated as intermediate products. The C-S bond as an intermediate tends to form elemental sulfur, while the S-O bond as an intermediate is likely to form H₂SO₄. For the AC₂ and AC₃ samples, there is no clear change in the carbon functional groups. After the thermal regeneration, the content of C-S bond in the blank sample significantly decreases. The bond-breaking needs endothermic, and thermal regeneration provides energy. For AC₁–AC₃ samples, the main change is reflected in the reduction of C=C and C-S bonds and the

| Samples   | C   | H   | N   | S   | O    |
|-----------|-----|-----|-----|-----|------|
| Fresh AC  | 79.10 | 1.19 | 0.99 | 0.34 | 18.38 |
| Blank     | 79.27 | 1.31 | 1.02 | 0.44 | 17.96 |
| AC₁       | 75.71 | 1.31 | 0.97 | 1.87 | 20.14 |
| AC₂       | 76.15 | 1.13 | 1.07 | 1.79 | 19.78 |
| AC₃       | 75.82 | 1.20 | 0.97 | 1.83 | 20.18 |

Fig. 1 S 2p peaks from XPS for the activated carbon samples
increase of the C=O and C-O bonds. The C=C bond reacts with H₂SO₄ to release SO₂. The C-S bond is unstable and easily decomposes to release elemental sulfur at high temperatures. The C=O and C-O bonds are more stable than the other carbon functional groups (Guo et al. 2013), so that the total amount of these two carbon functional groups changes little but their proportion increases. The decrease in the C=C bond is most obvious for AC₃, which is related to the fact that the highest H₂SO₄ content among the three samples is observed on AC₃. The content of C=C bond basically changes little due to the few sulfur compounds in the blank sample reacting with C=C bond.

As shown in Fig. 2b, compared with the blank sample, the C=O bond amount of AC₁ clearly decreases and the OH amount increases, due to the combination of the C=O bond with free H in H₂S to form OH bond (Li et al. 2019b). For AC₂ and AC₃, the OH amount obviously decreases, due to the formation of H₂SO₄ or H₂SO₃ through the combination of the OH site with SO₂. In the thermal regeneration process, COOH and OH can be decomposed below 450 °C and mainly from carboxyls, lactones, and anhydrides (Vivovilches et al. 2014), which is an important reason for the loss of the carbon functional groups, while the C=O bond amount increases significantly, due to their stable chemical properties.

To further illustrate the decomposition process of the sulfur products in activated carbon, in situ DRIFT spectra are carried out with the results shown in Fig. 2c, d. H₂SO₃ (872 cm⁻¹) and H₂SO₄ (1090 cm⁻¹) are observed in the adsorption process,
particularly for the AC 2 and AC 3 samples, but their amount decreases during the regeneration process. Due to the adsorption amount of acid SO 2, the alcohol (OH) (1240 cm⁻¹) decreases while alkyl ether (1020 cm⁻¹) increases in the AC 2 and AC 3 samples. In the regeneration process, the reduction of the S-O bond (1150 cm⁻¹) is significant in AC 3, representing the decomposition of sulfuric acid. Another important change is the decomposition of carboxylic acid (1080 cm⁻¹). Carboxylic acid on the activated carbon surface decomposes below 450 °C, which is an important reason for the reduction in the denitrification efficiency of the activated carbon after regeneration.

In the regeneration process, the chemical carbon consumption comes from the decomposition of oxygen-containing functional groups and the reaction of activated carbon with H 2SO 4. Carboxyls, lactones, and anhydrides with COOH and OH groups can be decomposed below 450 °C. The thermal decomposition of functional groups is independent of the type of sulfur-containing products. The thermal regeneration of sulfur-containing products results in the reduction of the C=C bond amount. The C=C bond reacts with H 2SO 4 to produce CO and CO 2.

**Effect of sulfur product regeneration on chemical carbon consumption**

Figure 3 shows the SO 2 concentration for the AC 1–AC 3 samples during the TPD process. The decomposition temperature range of H 2SO 3 is 150~300 °C, and H 2SO 4 decomposes at 300~450 °C (Lin et al. 2018). Therefore, the regeneration temperature is set at 450 °C for the complete desorption of SO 2. At approximately 380 °C, a main peak of the H 2SO 4 decomposition is observed. A shoulder peak of SO 2 desorption is observed in AC 2 at 150~300 °C because the H 2SO 3 decomposition temperature is lower than that of H 2SO 4 (Kim et al. 2019). The peak areas of AC 1–AC 3 are 37523, 46112, and 67321 in the range of 300~450 °C, basically proportional to the H 2SO 4 contents of 33.1%, 39.7%, and 60.7% calculated from the XPS spectra as given in Fig. 1. There are no clear differences between the total sulfur contents of the three adsorbed samples, while the concentration of the desorbed SO 2 from AC 1 is significantly lower than AC 2 and AC 3, indicating that most of the sulfur in AC 1 decomposes in the form of sulfur vapor instead of SO 2.

The results of elemental analysis of various samples after the TPD process are shown in Table 2. Compared with the data in Table 1, the sulfur and oxygen contents in AC 1–AC 3 samples decrease during the TPD process, due to the decomposition of the sulfur species and oxygen functional groups at high temperature (Lin et al. 2018). The sulfur content shows slight differences among the three samples, showing that the three samples have similar values of the total desorption amount of the sulfur species. However, clear differences among the three samples are observed for the oxygen content. The oxygen content of AC 1 is significantly higher than those of AC 2 and AC 3. Combined with the data in Table 1, there was no significant difference in oxygen content for AC 1–AC 3 samples after adsorption. Due to the different sulfur species on the surface of activated carbon, sulfur is released in different forms. The release of elemental sulfur is in the form of sulfur vapor, while the release of sulfate is in the form of SO 2, which will bring out a part of oxygen, resulting in the oxygen content of AC 2 and AC 3 being significantly less than that of AC 1. Moreover, the higher the SO 2 emission, the lower the oxygen content of activated carbon.

Figure 4 shows the results for the SO 2 desorption and chemical carbon consumption of the three samples during the regeneration process. The SO 2 desorption in AC 1 is much lower than that in AC 2 and AC 3, because the elemental sulfur desorption cannot be detected by FTIR. AC 1 has the smallest carbon consumption, because the release process of elemental sulfur will not cause carbon consumption. For AC 2, some H 2SO 3 can be decomposed directly at a lower temperature, thus reducing the release of CO and CO 2. AC 3 consumes the most carbon, mainly due to the reaction of sulfuric acid and carbon.

**Table 2**  Elemental analysis of the activated carbon samples after the TPD process (wt%)

| Samples | C     | H     | N     | S     | O     |
|---------|-------|-------|-------|-------|-------|
| Blank   | 86.12 | 1.97  | 0.61  | 0.39  | 10.91 |
| AC 1    | 86.16 | 1.67  | 1.09  | 0.44  | 10.64 |
| AC 2    | 87.23 | 1.81  | 1.37  | 0.41  | 9.18  |
| AC 3    | 88.02 | 1.77  | 1.01  | 0.52  | 8.68  |

Fig. 3  SO 2 concentration during the TPD process for the activated carbon samples
The carbon consumption of the blank sample can be used to calculate the decomposition of oxygen-containing functional groups during regeneration. As shown in Table 3, according to the comparison of the oxygen content between the activated carbon and blank sample, about 6% of the oxygen-containing functional groups are consumed in the regeneration process. For AC1, the total carbon consumption during regeneration is 0.28 mmol/g, of which 75% comes from the thermal decomposition of oxygen-containing functional groups and 25% originates from the reaction between C and H2SO4. For the AC3 sample, the total carbon consumption during regeneration is 0.68 mmol/g, including 31% from its own thermal decomposition and 69% from its reaction with H2SO4. No matter what sulfur species are on the surface of activated carbon, the thermal decomposition process of oxygen-containing functional groups on activated carbon will not be affected. The desorption of elemental sulfur consumes less oxygen and carbon functional groups, reducing the chemical carbon consumption by 59.8% than H2SO4. In AC3, the carbon consumption caused by the regeneration of sulfur-containing products is more than twice that caused by the decomposition of oxygen-containing functional groups, which indicates that the most important carbon consumption for the activated carbon used is caused by the reaction of C and H2SO4.

Unlike SO2 released by H2SO4 and H2SO3, sulfur vapor released by elemental sulfur cannot be determined during the desorption process. To further evaluate the morphology of sulfur products, DTG characteristics were used to measure the total weight loss at various temperature ranges, with the results shown in Fig. 5. The peak at 350 °C represents the decomposition of H2SO4, while elemental sulfur directly sublimates at approximately 380 °C. Based on the temperature peak position, AC1 mainly contains elemental sulfur and a small amount of H2SO4, and AC2 contains less H2SO4 than AC3. H2SO4 and a small amount of elemental sulfur are found on the surface of AC3. The differences between the peak area of DTG curves and that of SO2, CO, and CO2 content curves are the content of elemental sulfur. And elemental sulfur in AC1 is the highest, which is consistent with the results in Fig. 1. It can be concluded from the DTG curves that the elemental sulfur sublimates at 350–400 °C, which is of great significance to guide the design for industrial flue gas purification by activated carbon process.

Electron Spin Resonance was used to calculate the average chain length of sulfur by dividing the number of electron spin (Terada et al. 2020). The ESR spectrogram is shown in Fig. S3.

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**Table 3** SO2 recovery and carbon consumption of the AC samples

| Samples | S (mmol/g) | Carbon consumption (mmol/g) |
|---------|-----------|-----------------------------|
|         | Adsorption (H2S and SO2) | Desorption (SO2) | CO | CO2 | Total | C/S |
| Blank   | 0         | 0                            | 0.04 | 0.17 | 0.21  | —   |
| AC1     | 0.76      | 0.15                         | 0.06 | 0.22 | 0.28  | 0.45 |
| AC2     | 0.73      | 0.39                         | 0.16 | 0.44 | 0.60  | 1.00 |
| AC3     | 0.77      | 0.36                         | 0.20 | 0.48 | 0.68  | 1.12 |

*Blank refers to the blank activated carbon without adsorption*
Fig. 5  DTG curves for the absorbed AC

Fig. 6  Morphological changes of elemental sulfur during adsorption-regeneration process
where \( E \) (in spins per gram) is the amount of electron spin of samples and \( N_A \) \((6.022 \times 10^{23} \text{ mol}^{-1})\) is Avogadro constant. It is difficult to test the electron spin of activated carbon because of its magnetism. So, the results of elemental sulfur were used to characterize the properties of elemental sulfur produced by adsorption on activated carbon, as shown in Fig. 6. When the elemental sulfur rises from room temperature to 150 °C, the chain length of sulfur has no obvious change, and the average value is about \( 2 \times 10^6 \). It is difficult for orthorhombic sulfur to exist at 150 °C; the sulfur form at this temperature is monoclinic sulfur \( (S_8) \) \( \text{Tera} \text{da et al. 2020} \). Each sulfur atom forms a covalent single bond with the other two sulfur atoms in the sp\(^3\) hybrid orbit \( \text{Brandi et al. 2019} \). When the temperature continues to rise up to 254 °C, the electron spin number of sulfur is close to 0; the \( S_8 \) ring structure breaks into infinitely long chain molecules \( (S_\infty) \). Above 254 °C, the long chain sulfur breaks into small molecules, such as \( S_6 \) and \( S_2 \). At 400 °C, the sulfur becomes vapor, and the volume fraction of each component for sulfur vapor is 3.7% for \( S_2 \), 56.4% for \( S_6 \), and 39.9% for \( S_8 \).

Table 4 shows the reactions of sulfur-containing substances with activated carbon in the adsorption-regeneration process. C(O) represents the oxygen functional groups on the activated carbon surface.

The carbon consumption partly depends on the existence form of sulfur-containing products, in addition to the thermal decomposition of functional groups. The desorption of elemental sulfur consumes less oxygen and carbon functional groups, with 59.8% less chemical carbon consumption than \( \text{H}_2\text{SO}_4 \). The carbon consumption caused by the regeneration of sulfur-containing products is less than that by the decomposition of functional groups with elemental sulfur as the main products.

### Influence of sulfur product regeneration on physical carbon abrasion

To investigate the influence of sulfur product regeneration on the AC physical structure, the pore structures were analyzed before and after the regeneration. The results are shown in Table 5. In comparison with the blank sample, the specific surface area and pore volume of AC\(_1\)–AC\(_3\) clearly decrease.

### Table 4 Reactions for adsorption-regeneration process of sulfur-containing substances on activated carbon

| Process               | Change of reactants                                      | Reaction                                      | Participating functional groups | No. |
|-----------------------|----------------------------------------------------------|------------------------------------------------|---------------------------------|-----|
| Adsorption            | Adsorption and oxidation of SO\(_2\)                   | \( \text{SO}_2 \rightarrow \text{H}_2\text{SO}_3 \) | OH                              | (1) |
|                       |                                                          | \( \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \) |                                 | (2) |
| Oxidation of H\(_2\)S |                                                          | \( \text{H}_2\text{S} \rightarrow S(s) \)       | \( \text{C} = \text{O}, \text{C} = \text{C} \) | (3) |
|                       |                                                          | \( \text{H}_2\text{S} \rightarrow \text{H}_2\text{SO}_3 \) | \( \text{Intermediate product: C-S, S-O} \) | (4) |
|                       |                                                          | \( \text{H}_2\text{S} \rightarrow \text{H}_2\text{SO}_4 \) |                                 | (5) |
| Regeneration           | Regeneration of sulfur products                         | \( \text{H}_2\text{SO}_4 + \text{C} \rightarrow \text{SO}_2 + \text{CO} + \text{H}_2\text{O} \) | \( \text{C}=\text{C} \)         | (6) |
|                       |                                                          | \( 2\text{H}_2\text{SO}_4 + 2\text{C} \rightarrow 2\text{SO}_2 + \text{CO}_2 + 2\text{H}_2\text{O} \) |                                 | (7) |
|                       |                                                          | \( \text{H}_2\text{SO}_3 \rightarrow \text{SO}_2 + \text{H}_2\text{O} \) |                                 | (8) |
|                       |                                                          | \( S(s) \rightarrow S(g) \)                     | \( \text{C}(\text{O}) \rightarrow \text{CO}_2 \) | (9) |
|                       | Decomposition of carbon-functional groups               | \( \text{C}(\text{O}) \rightarrow \text{CO} \)  | \( \text{Carboxyls, lactones, and anhydrides} \) | (10) |

\( L = \left( \frac{1}{32.07} \times N_A \right) / \left( E \times \frac{1}{2} \right) \)
These deposits will cover the pore entrance and surface of activated carbon, resulting in the loss of active sites. Moreover, the specific surface area of AC1 decreases by 11%, and that of AC3 decreases by 20%. This phenomenon is ascribed to the different volumes of elemental sulfur and H2SO4 under the premise of the same sulfur content. The volume of elemental sulfur is 13.6 cm3/mol, while that of sulfuric acid is 53.5 cm3/mol, and that of H2SO3 is 79.6 cm3/mol (Lau et al. 2017). Therefore, when elemental sulfur rather than H2SO4 is deposited on the activated carbon surface, the decrease in the specific surface area is not obvious. After thermal regeneration, both the specific surface area and pore volume increase because of the partial decomposition of the functional groups and the desorption of sulfur-containing substances. The pore size of the activated carbon is restored to the level of the fresh activated carbon, and even increases after the regeneration.

The graphite microcrystalline structure of the AC samples before and after regeneration is shown in Fig. 7. Raman spectra of all samples display two peaks including the disorder (D) peak at 1360 cm−1 reflecting the structural defects and the graphite (G) peak at 1600 cm−1 reflecting the sp2 carbon atoms in the graphene sidewalls. The ratio of the peak intensity (I_D/I_G) represents the degree of disorder in the graphite microcrystalline structure on activated carbon (Zhang et al. 2019). The D and G peaks of various AC samples are basically the same prior to regeneration. The D peaks of AC1–AC3 samples clearly increase after regeneration, while the G peak does not change much, so that the I_D/I_G value increases significantly, particularly for AC3. In the high temperature of the regeneration process, the oxygen-containing functional groups on the activated carbon easily decompose, and the lattice structure tends to be regular.

From the macroscopic point of view, the activated carbon structure can also be characterized by compressive strength and wear resistance, which are tested before and after regeneration, with results shown in Fig. 8. There is little difference between the wear resistance values before and after regeneration, while the compressive strength clearly decreases.

| Sample | BET (m2/g) | V_m (mL/g) | V_t (mL/g) |
|--------|------------|------------|------------|
|        | Be-re      | Af-re      | Be-re      | Af-re      | Be-re      | Af-re      |
| Fresh AC | 196        | 0.070      | 0.087      |            |            |
| Blank  | 198        | 0.070      | 0.091      | 0.096      |            |
| AC1    | 175        | 0.065      | 0.073      | 0.076      | 0.096      |
| AC2    | 161        | 0.059      | 0.070      | 0.076      | 0.093      |
| AC3    | 157        | 0.059      | 0.070      | 0.069      | 0.093      |

*Be-re is the abbreviation of before-regeneration. Af-re is the abbreviation of after-regeneration.

Fig. 7 Raman spectra for various AC samples before and after regeneration
especially for the AC$_2$ and AC$_3$ samples, indicating that the reaction of C and H$_2$SO$_4$ destroys the integrity of the carbon structure. The compressive strength and wear resistance decrease on regenerated activated carbon, leading to the increase in the amount of small granular activated carbon, and finally increase the physical carbon abrasion.

**Total carbon consumption in engineering applications**

The total carbon consumption in engineering applications includes chemical carbon consumption and physical carbon abrasion. In this work, two factories using activated carbon technology for flue gas purification were investigated. One is for sintering flue gas purification to capture SO$_2$, and the other is for coke oven flue gas purification to simultaneously remove SO$_2$ and H$_2$S. The results are shown in Table 6.

For sintering flue gas purification, the total carbon consumption is about 55% of the total charge per year; among them, the physical carbon abrasion is about 38%, and the chemical carbon consumption is about 17%. The physical carbon abrasion is twice more than chemical carbon consumption. The total carbon consumption is approximately 48% for coke oven flue gas, lower than that for sintering flue gas. The high content of H$_2$S depresses the carbon consumption in the regeneration process compared with the same content of SO$_2$.

In order to reduce carbon consumption, the following strategies can be considered. Use air screen sorting devices to reduce physical carbon abrasion. With the increase of operation time, the particle size of activated carbon becomes smaller and smaller. The small particles and dust fill in the gap of activated carbon bed increasing the resistance of flue gas. An efficient balance vibrating screen in the activated carbon conveying system is commonly used to screen out small particles, but this measure will undoubtedly greatly increase the physical carbon abrasion between the particles and particle with vibrating screen. In order to solve this problem, an air screen sorting device for activated carbon was developed in the project. Driven by the upstream hot air flow, the dust and small particles in the activated carbon were gradually fluidized, suspended, and finally separated under the traction of the upstream air flow. This process reduces the collision and friction between the particles and vibrating screen and then greatly reduces the physical carbon abrasion.

Select a high-quality activated carbon to reduce chemical carbon consumption. In engineering, the main quality index of activated carbon includes sulfur capacity, wear resistance, compressive strength, ignition point, and particle size distribution. In this work, it is found that elemental sulfur generated by H$_2$S can reduce the chemical carbon consumption of activated carbon. Therefore, the activated carbon with less C=O bond should be selected under the premise of ensuring the

| Table 6 Comparison of total carbon consumption between sintering flue gas and coke oven flue gas |
|---------------------------------|------------------|-------------------|
| Sintering flue gas              | Coke oven flue gas |
| Total gas volume (Nm$^3$/h)     | 2,800,000        | 300,000           |
| Inlet SO$_2$ (ppm)              | 200–300          | 50–100            |
| Inlet H$_2$S (ppm)              | —                | 150–200           |
| Outlet SO$_2$ (ppm)             | 20               | 10                |
| Outlet H$_2$S (ppm)             | —                | 15                |
| Total AC loading (t)            | 12,000           | 2500              |
| Total AC consumption (t/a)      | 6600             | 1200              |
| Ratio of carbon consumption (%) | 55%              | 48%               |
| Physical carbon abrasion (%)    | 38%              | 35%               |
| Chemical carbon consumption     | 17%              | 13%               |
above quality index, which can effectively reduce the production of \( \text{H}_2\text{SO}_4 \) and greatly reduces the chemical carbon consumption.

**Conclusions**

\( \text{H}_2\text{S} \) can react with the C=C bond on the activated carbon surface to form C-S bond as an intermediate state, followed by the formation of elemental sulfur. It directly sublimates at approximately 380 °C, about 30 °C higher than the decomposition temperature of \( \text{H}_2\text{SO}_4 \). So, the regeneration temperature should be determined according to the sublimation temperature of elemental sulfur in the engineering application. At the adsorption temperature, the state of elemental sulfur is monoclinic sulfur in the form of \( \text{S}_8 \) ring molecules. When the activated carbon is regenerated, the temperature rise first causes the \( \text{S}_8 \) ring structure to break into infinitely long chain molecules (\( \text{S}_\infty \)). When the activated carbon is heated above 254 °C, the long chain sulfur breaks into small molecules. At 400 °C, the sulfur becomes vapor, and the volume fraction of each component for sulfur vapor is 3.7% for \( \text{S}_2 \), 56.4% for \( \text{S}_6 \), and 39.9% for \( \text{S}_8 \). The desorption process of elemental sulfur consumes less oxygen and carbon functional groups, reducing the chemical carbon consumption by 59.8% than \( \text{H}_2\text{SO}_4 \); due to the slight effect on the disordered graphitic structure, its compressive strength is reduced less.

\( \text{H}_2\text{S} \) also reacts with the C=O bond to form \( \text{H}_2\text{SO}_3 \) and \( \text{H}_2\text{SO}_4 \). The decomposition of \( \text{H}_2\text{SO}_3 \) does not require carbon consumption. The deposited \( \text{H}_2\text{SO}_4 \) reacts with the C=C bond to generate \( \text{SO}_2 \), which is the cardinal reaction of the thermal regeneration. In addition, \( \text{H}_2\text{SO}_4 \) decomposition improves the ratio of the disordered graphitic structure. About 6% of the oxygen-containing functional groups are consumed in the regeneration process, and most of these functional groups are carboxyls, lactones, and anhydrides. The carbon consumption caused by the regeneration of sulfur-containing products is more than that caused by the decomposition of oxygen-containing functional groups.

From the data of the engineering project, the total carbon consumption of coke oven flue gas is slightly lower than that of sintering flue gas. \( \text{H}_2\text{S} \) will depress the carbon consumption in the thermal regeneration process compared with \( \text{SO}_2 \). To reduce carbon consumption, the following two strategies can be considered. Use air screen sorting devices to reduce the collision between activated carbon and vibrating screen and then significantly reduce the physical carbon abrasion. Select the activated carbon with less C=O bond to reduce the production of \( \text{H}_2\text{SO}_4 \) and then greatly reduce the chemical carbon consumption.

**Supplementary Information** The online version contains supplementary material available at [https://doi.org/10.1007/s11356-021-14914-2](https://doi.org/10.1007/s11356-021-14914-2).
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