Regeneration performance and carbon consumption of semi-coke and activated coke for SO$_2$ and NO removal

Song Ding$^{1,2}$, Yuran Li$^2$, Tingyu Zhu$^{1,2,*}$, Yangyang Guo$^2$

1. School of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550025, China. E-mail: sding@ipe.ac.cn
2. National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

**ABSTRACT**

To decrease the operating cost of flue gas purification technologies based on carbon-based materials, the adsorption and regeneration performance of low-price semi-coke and activated coke were compared for SO$_2$ and NO removal in a simulated flue gas. The functional groups of the two adsorbents before and after regeneration were characterized by a Fourier transform infrared (FTIR) spectrometer, and were quantitatively assessed using temperature programmed desorption (TPD) coupled with FTIR and acid-base titration. The results show that semi-coke had higher adsorption capacity (16.2% for SO$_2$ and 38.6% for NO) than activated coke because of its higher content of basic functional groups and lactones. After regeneration, the adsorption performance of semi-coke decreased because the number of active functional groups decreased and the micropores increased. Semi-coke had better regeneration performance than activated coke. Semi-coke had a larger SO$_2$ recovery of 7.2% and smaller carbon consumption of 12% compared to activated coke. The semi-coke carbon-based adsorbent could be regenerated at lower temperatures to depress the carbon consumption, because the SO$_2$ recovery was only reduced a small amount.

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**Keywords:**
Functional groups  
SO$_2$ recovery  
Adsorption  
Carbon consumption

**Introduction**

The combustion of coal and other fossil fuels emits many pollutants, such as SO$_2$ and NO$_x$. To decrease the amounts of these pollutants, many flue gas purification technologies have been developed. Those using carbon-based materials are considered some of the best flue gas purification technologies (Tsui and Shiraishi, 1997; Zhu et al., 2000; Li et al., 2012; Izquierdo et al., 2003; Guo et al., 2013; Hou et al., 2009). These technologies use activated coke, activated carbon or activated carbon fiber as the adsorbent for SO$_2$ and NO$_x$ removal, since these materials possess both adsorption capacity for SO$_2$, NO$_x$, dioxins and other pollutants based on physical-sorption and/or chemisorption, and catalytic activity for NO$_x$ reduction with NH$_3$. Moreover, no wastewater or secondary pollutants are produced, and SO$_2$ can be effectively recovered by the reaction of H$_2$SO$_4$ with carbon on the surface when the adsorbents are heated (Guo et al., 2008; Zhang et al., 2012b).

However, these flue gas purification technologies with carbon-based materials have two key problems, namely, high operating cost and high heat consumption. For example, when activated coke (approximately 5000 CNY/ton) is used as the adsorbent, the cost of the activated coke is 50%–70% of the total operating cost (Zhang and Xu, 2012). The regeneration temperature is usually 400°C, requiring a large amount of heat. Therefore, the main research thrust for flue gas purification technologies with carbon-based materials is to find a low-price carbon-based material as the adsorbent in...
order to reduce the cost, improve the adsorption performance by modification, and lower the regeneration temperature to save heat. Activated coke has been used in many plants, because its price is cheaper than that of activated carbon. To improve the de-SO₂ and de-NO performance of activated coke, the coke is modified by loading with metal oxides, such as those of V, Co, Mo and Fe (Liu and Liu, 2013; Ma et al., 2003, 2008; Xing et al., 2008). To save energy consumption, the regeneration progress of spent activated coke has also been investigated through changes in the heating method or the gas medium during regeneration (Zhang et al., 2012b; Guo et al., 2007a, 2007b; Xing et al., 2007).

Semi-coke (approximately 1000 CNY/ton) is prepared from non-caking coal or weakly caking coal, carbonized at 500-700°C. Semi-coke is richer in surface functional groups than activated coke, which is treated by oxidation in order to increase the specific surface area. Although the preparation processes are different, semi-coke and activated coke have similar physical and chemical properties. It was reported that low-price lignite semi-coke has an adsorption capacity for mercury (Zhang et al., 2012a) that is the same as that of activated coke. Therefore, to explore the application potential of semi-coke for SO₂ and NO removal, the adsorption and regeneration performances of semi-coke and activated coke were compared. The promotional effect of the physical and chemical properties of the materials on SO₂ and NO adsorption was investigated. Carbon consumption and SO₂ recovery were also studied to compare the regeneration performance.

### Table 2 – Pore properties of adsorbents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET} (m²/g)</th>
<th>Vₘ (mL/g)</th>
<th>Vₜ (mL/g)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated coke</td>
<td>88.400</td>
<td>0.0366</td>
<td>0.0703</td>
<td>1.572</td>
</tr>
<tr>
<td>Semi-coke</td>
<td>59.879</td>
<td>0.0244</td>
<td>0.0579</td>
<td>1.419</td>
</tr>
</tbody>
</table>

S_{BET}: BET surface area; Vₘ: micropore volume; Vₜ: total pore volume; D: average pore diameter.

### 1. Experiments

#### 1.1. Materials and characterization

Semi-coke from the Sanjiang Coal Chemical Plant (Shanxi, China) and activated coke from the Xinhua Chemical Plant (Taiyuan, China) were used. The two materials were crushed, and the particles were sieved through 2-60 mesh (0.25-0.85 mm). These particles were washed by deionized water and then dried at 105°C for 24 hr after filtration. Elemental analysis was performed on an Analyzer (Vario El cube, Elementar, Germany), and the results are shown in Table 1.

The pore properties of adsorbents were determined at –196°C through nitrogen adsorption (Autosorb-IQ, Quantachrome, USA). The BET (Brunauer–Emmett–Teller) surface area (S_{BET}), micropore volume (Vₘ), and average pore diameter (D) were calculated by the Brunauer–Emmett–Teller equation, Dubinin–Radushkevich equation and Horvath–Kawazoe equation, respectively. The total pore volumes (Vₜ) were directly calculated. The results are shown in Table 2.

Functional groups of adsorbents were characterized by a FTIR spectrometer (Nicolet 6700, Thermo, Waltham, Massachusetts, USA). Absorption was measured over the range from 400 to 4000 cm⁻¹ with a resolution of 2 cm⁻¹. The background spectrum was obtained by using KBr as a blank. The ratio of sample to KBr was approximately 1:1000, and the samples were scanned 8 times. The functional groups that contained oxygen were analyzed by temperature programmed desorption (TPD) coupled with Fourier transform infrared (FTIR), and the basic functional groups were determined by acid–base titration.

The SO₂ recovery is the ratio of total SO₂ released during regeneration to total SO₂ adsorbed during adsorption. Carbon consumption is the total C amount of CO and CO₂ emitted during regeneration (mmol/g).

#### 1.2. Experimental system and reaction conditions

The experimental system is composed of a fixed-bed reactor, heating temperature control system, simulated flue gas system and detection system. The reactor is a quartz tube with a sintered silica plate in the middle for loading the adsorbents. The diameter of the tube is 20 mm, and the length is 520 mm. The heating temperature control system is a resistance furnace connected to a temperature controller to adjust the temperature. After passing through flow-meters, gases, such as SO₂, NO, NH₃, O₂ and N₂, were mixed in a jar and then entered the reactor. The water vapor was produced by evaporating water in a U-tube and was carried by N₂. The amount of water vapor can be calculated by the Antoine equation and the flow of N₂. The composition of the simulated flue gas was 0.1 mol% SO₂, 0.05 mol% NO, 0.05 mol% NH₃, 5 mol% H₂O, 5 mol% O₂, and balance N₂.

During adsorption, the adsorbent was maintained for 90 min in the simulated flue gas, the temperature was 150°C, the total flow was 300 mL/min, and the gas hourly space velocity (GHSV) was approximately 5700 hr⁻¹. After adsorption, the adsorbent was regenerated by heating. The regeneration
temperature was ramped from 150 to 400°C at 5°C/min and then was maintained at 400°C for 40 min in N₂. The gas flow was 180 mL/min during regeneration. The adsorption experimental parameters for regenerated absorbents were identical to the initial experimental adsorption parameters. The concentrations of components in the inlet and outlet were measured online by a FTIR spectrometer (Tensor 27, Bruker, Karlsruhe, Baden-Württemberg, Germany).

2. Results and discussion

2.1. Adsorption performance

Fig. 1 shows the breakthrough curves of the two adsorbents. The SO₂, NO and NH₃ breakthrough concentrations of semi-coke were lower than those of activated coke. Through integration and calculation, the de-SO₂ and de-NO capacities of activated coke were found to be 11.70 and 0.88 mg/g, respectively, and the de-SO₂ and de-NO capacities of semi-coke were 13.60 and 0.88 mg/g, respectively, and the adsorption performance for SO₂ and NO than activated coke. The result indicates that semi-coke had better adsorption performance for SO₂ and NO than activated coke. The result shows that the CO concentration of semi-coke is smaller than that of activated coke, and the CO₂ concentration of semi-coke is greater than that of activated coke. Because the thermal stability of different functional groups varies, when the temperature is increased, the active functional groups will decompose into CO and/or CO₂. Normally, CO₂ derives from carboxyl, anhydride and lactone and CO derives from anhydride, phenol, carbonyl and quinonyl (Figueiredo et al., 1999; Figueiredo and Pereira, 2010). By integrating the CO and CO₂ curves of the two adsorbents, the amounts of functional groups on the two adsorbents vary in decreasing order according to lactone, carboxyl, quinonyl, phenol, carbonyl and anhydride. Between semi-coke and activated coke, the difference is in the amounts of lactone and carbonyl. The lactone content of semi-coke is 92% higher than that of activated coke, but the carboxyl content of semi-coke is lower than that of activated coke. These results are in agreement with the IR analysis.

Fig. 3a shows the TPD curves of the two adsorbents. It can be seen that the CO concentration of semi-coke is smaller than that of activated coke, and the CO₂ concentration of semi-coke is greater than that of activated coke. Therefore, semi-coke possesses high removal efficiencies for SO₂ and NO due to its more plentiful functional groups or larger pore size than activated coke.

The IR absorption spectra of the two adsorbents are shown in Fig. 2. The two adsorbents show a number of absorption peaks in the range from 400 cm⁻¹ to 4000 cm⁻¹. According to previous studies (Ning, 2010; Shafeeyan et al., 2010), the peaks at 3600–3200 cm⁻¹ can be assigned to the O–H stretching vibrations of alcohol, phenol, water and the N–H stretching vibrations of –NH and –NH₂; the peaks at 3000–2800 cm⁻¹ are assigned to the C–H stretching vibrations of –CH₂ and –CH₃; the peaks at 1700–1585 cm⁻¹ are assigned to the C=O stretching vibrations of carboxyl and the C=C stretching vibrations of benzene; the peaks at 1440–1395 cm⁻¹ are assigned to the C≡O stretching vibrations of carboxyl; and the peaks at 1200–1000 cm⁻¹ are assigned to the C–O stretching vibrations of alcohol, ether and anhydride. Comparing the spectra of the two adsorbents, the peaks at 1435 and 1628 cm⁻¹ are significantly different. The reason is that semi-coke has more –COO⁻ and less C=O than activated coke.

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Fig. 3b shows the TPD curves of the two adsorbents. It can be seen that the CO concentration of semi-coke is smaller than that of activated coke, and the CO₂ concentration of semi-coke is greater than that of activated coke. Therefore, semi-coke possesses high removal efficiencies for SO₂ and NO due to its more plentiful functional groups or larger pore size than activated coke.

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By analyzing the adsorbents by acid–base titration, the result shows that the basic functional group concentrations of semi-coke and activated coke are 1.055 and 0.609 mmol/g.
respectively. The basic functional group content of semi-coke is 73.2% higher than that of activated coke. Additionally, C–O–C in the lactonic structure plays an important role in SO₂ adsorption and may be the active center of the desulfurization on activated semi-coke (Ju et al., 2005). Therefore, the abundant basic and acidic functional groups on semi-coke promoted the SO₂ and NO removal.

### 2.2. Re-adsorption performance after regeneration

The breakthrough curves of adsorbents after regeneration are shown in Fig. 4. Through integration and calculation, the adsorption capacities of activated coke after regeneration are found to be 12.07 mg/g for SO₂ and 0.88 mg/g for NO. The adsorption capacities of semi-coke after regeneration are 12.75 mg/g for SO₂ and 0.6 mg/g for NO. The de-SO₂ capacity of semi-coke after regeneration is 5.6% higher than that of activated coke, but the de-NO amount of semi-coke after regeneration is 31.8% lower than that of activated coke. Comparing the adsorption capacities of semi-coke before and after regeneration, those after regeneration are 6.3% smaller for SO₂ and 50.8% smaller for NO than those of fresh semi-coke. It is tentatively proposed that the pore structure or chemical properties of the adsorbents changed during thermal regeneration; for example, the decomposition of lactone and carboxyl possibly took place.

Infrared adsorption spectra of adsorbents before and after regeneration are shown in Fig. 5. The spectra display significant differences at 1628 and 1435 cm⁻¹ for the two adsorbents. The carboxyl content of activated coke did not obviously change, but the carboxyl content of semi-coke decreased.

Fig. 6 shows the micropore volumes and pore size distributions of the two adsorbents before and after regeneration. After
regeneration, the micropore volumes of semi-coke and activated coke increased by 25.8% and 15.9%, respectively, because of the opening of closed pores and the expansion of micropores. The range of pore size distribution of activated coke did not change, but the range of pore size distribution of semi-coke widened because of increasing numbers of micropores, the pore size of which is less than 0.42 nm. According to previous studies (Raymundo-Piñero et al., 2000, 2003; Guo et al., 2001; Xu et al., 2006), the SO2 and NO equivalent diameters are in the range of 0.28–0.35 nm and 0.11–0.31 nm, respectively, and the optimal pore size of activated coke for removal of SO2 was reported to be 0.7 nm. Therefore, a wide range of pore size is adverse for the adsorption and oxidation of SO2. The NO adsorption amount of an adsorbent is determined by its surface chemical properties. Although the pore volume of semi-coke increases after regeneration, the increased volume is mostly contributed by micropores. Smaller pore size hinders the dispersion of SO2. Therefore, the adsorption capacities of semi-coke are reduced for SO2 and NO because of the decomposition of active functional groups and the increase of micropores, which are not beneficial to SO2 adsorption.

2.3. Carbon consumption

Fig. 7 shows the regeneration curves of the two adsorbents. SO2, NO and NH3 curves are shown in Fig. 7a, and CO and CO2 curves are shown in Fig. 7b. The trends of the SO2, NO, NH3, CO and CO2 concentrations were observed during regeneration, but NO was not detected. This was because NO mainly reacted with NH3 through SCR and formed N2, and SO2 transformed into H2SO4, then some H2SO4 reacted with NH3 and generated ammonium sulfates on the adsorbent surface. During thermal regeneration, H2SO4 and ammonium sulfates can react with carbon on the surface, releasing SO2, NH3, CO and CO2 with the rising temperature.

Fig. 7a shows that with increasing temperature, the SO2 concentrations of the two adsorbents first increase and then decrease. The SO2 concentration is at a maximum when the temperature is approximately 240°C. Through integrating the SO2 concentration curves, the amount of SO2 released for semi-coke was found to be more than that for activated coke. During the regeneration process, the SO2 recovery ratios of semi-coke and activated coke were 69.6% and 62.4%, respectively.

Fig. 7b shows that the CO concentration increases with increasing temperature, then the concentration suddenly drops at 400°C. This result indicates that CO is derived from active functional groups that have poor thermal stability. Under 325°C, the trend of the CO2 concentration is similar to that of the SO2 concentration, which increases quickly and then decreases. This result indicates that CO2 is mainly derived from the reaction of C with H2SO4 or ammonium sulfates. When the temperature reaches 325°C, the CO2 concentration gradually increases with increasing temperature and suddenly drops at 400°C. CO2 is mainly derived from the decomposition of active functional groups from 325 to 400°C.

The results of the integration of CO, CO2 and SO2 curves during regeneration are shown in Table 3. When 1 mol SO2 is released, the carbon consumption of semi-coke and activated coke is 0.8 and 0.91 mol, respectively. The carbon consumption of semi-coke is 12% smaller than that of activated coke.

Fig. 8 shows the SO2 recovery ratios and carbon consumption of the two adsorbents during regeneration at temperatures from 150 to 400°C. The initial decomposition temperature is 200°C. As the temperature rises, the SO2 recovery ratios of the two adsorbents first increase quickly and then slowly, and the carbon consumption increases throughout the entire course.

<table>
<thead>
<tr>
<th>Table 3 – Carbon consumptions of the adsorbents during regeneration.</th>
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<tr>
<td></td>
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<tr>
<td>Activated coke</td>
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<tr>
<td>Semi-coke</td>
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</tbody>
</table>
The SO₂ recovery ratios of semi-coke and active coke at 350°C (64.6% and 54.4%, respectively) are 4.3% and 5.1% smaller than at 400°C (68.9% and 59.5%, respectively). The carbon consumptions of semi-coke and active coke at 350°C (0.069 and 0.054 mmol/g, respectively) are 23.3% and 27.0% smaller than at 400°C (0.090 and 0.074 mmol/g, respectively). Therefore, to depress the decomposition of active functional groups and reduce the carbon consumption, the adsorbents that adsorbed SO₂ could be regenerated at lower temperatures, and the SO₂ recovery would only slightly decrease.

3. Conclusions

Semi-coke shows better adsorption performance for SO₂ and NO than activated coke, because it is richer in basic functional groups and lactones. After regeneration, the adsorption capacities of semi-coke decreased by 6.3% for SO₂ and 50.8% for NO. This decrease occurred because the active functional groups on the semi-coke surface decreased and the micropores, which are not beneficial to SO₂ dispersion, increased. The adsorption capacity of activated coke did not change, because the micropores, which are beneficial to SO₂ dispersion, were increased as a result of thermal regeneration and promoted SO₂ adsorption, despite the fact that the number of active functional groups on activated coke decreased. However, the adsorption capacity of semi-coke for SO₂ was 5.6% higher than that of activated coke.

Semi-coke displayed better regeneration performance than activated coke. After regeneration, the SO₂ recovery ratios of semi-coke and active coke were increased as a result of thermal regeneration and the SO₂ recovery would only slightly decrease.

Acknowledgments

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