A New Flue Gas Activation Process for SO₂ Removal with Activated Coke in Coal Power Plant*

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Abstract

The overall objectives of this study were to use waste flue gas as the activation gas to produce desulfurizers with industrial-scale size, to find the appropriate activated coke and the optimal preparation method, and to determine the operating conditions for the activated coke preparation. The effects of H₂O, CO₂ and O₂ contents in the flue gas were investigated to determine the optimal operating conditions. The results showed that the higher the content of carbon, volatile and calcium oxide (THC) in a coal was, the better the Brunauer-Emmett-Teller (BET) surface area and the pore volume are due to the increased activating temperature and decreased particle size. The activated coke, loaded with coal tar and finally activated with the flue gas at 800 °C, exhibited the best desulfurizing performance with a sulfur retention of about 101mg-SO₂/g-activated coke at a reaction temperature of 100 °C. The mechanism for SO₂ removal by activated coke shows that the BET surface area, pore volume and THC have a significant influence on SO₂ removal efficiency.

Key words: Flue Gas, Exhaust Gas, Desulfurization, Activated Coke, Power Plant

1. Introduction

Sulfur dioxide (SO₂) emitted in the combustion of fossil fuels is one of the key precursors to acid rain, a major air pollutant. It can cause many serious problems such as respiratory disease in humans in developing countries although the once-through non-regenerative wet flue gas desulfurization (FGD) processes, based mainly on limestone scrubbing, are frequently used. Wet processes require enormous volumes of water and costly facilities for purifying the wastewater. Semi-dry processes still need large volumes of water for a high desulfurization rate. Dry and regenerable FGD technologies are expected to be increasingly preferred, because it, compared with limestone scrubbing, offers a number of advantages: (1) a small sorbent make-up, (2) generation of relatively small amount of by-products, (3) recovery of sulfur as useful sulfur-containing products, (4) simultaneous removal of SO₂ and NO_x, (5) elimination of stack gas reheating and large water consumption ^{(1), (2)}. We attempted to develop a novel dry-desulfurization process by using activated coke reaction in gas phase to realize a high SO₂ removal efficiency under dry

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condition. The dry desulfurization, denitrification and air toxics removal process using activated coke was originally researched and developed during the 1960s by Bergbau Forschung (BF). It is called Deutsche Montan Technologies in Germany ⁽³⁾. From 1992, Mitsui Mining (Japan) developed a technology to produce activated coke used in the dry DeSOx/DeNOx/Air Toxics removal process based on the activated coke ⁽⁴⁾. The process, low-temperature DeSOx/DeNOx/Air Toxics removal system, was developed over many years, culminating with both pilot and demonstration plants. These tests have proven the system's capability of removing over 99% of the SOx. This activated coke has a surface area of 150-500m²/g that is less than that of conventional activated carbon. The catalytic activity for oxidative adsorption of SO₂ and NO is at 100-200°C. The quantity of SO₂ adsorbed is 45-110mg-SO₂/g-activated coke.

The overall objectives of this study were to use waste flue gas as the activation gas to produce desulfurizers (activated coke) with sizes of commercial interest ($\Phi 0.8 \times 1.2$ cm), to find the appropriate activated coke and the optimal preparation method, and to determine the operating conditions for the activated coke preparation in this work.

2. Nomenclature

k	constant of reaction rate
n	constant
P	pressure (Pa)
P ₀	saturation pressure of N ₂ (Pa)
Pr	system pressure (atm)
R _g	gas constant (J/ (mol •K))
r	reaction rate (%/hr)
T	temperature (K)
t	reaction time (s)
y	gas concentration (mole fraction)

3. The proposal of the new dry desulfurization process

A schematic of the activated coke preparation and SO₂-removal process is provided in Fig.1. This novel process consists of three sections: coal fired boiler (from 1 ~ 6), activated coke preparation (from 13~16), and SO₂ adsorption and activated coke regeneration (from 7~12). This paper only introduces the latter two parts process.

3.1. Activated coke preparation section

This section consists of three stages in activated coke preparation. First, the flue gas moves continuously from the boiler to the separator 16. The temperature of flue gas is about 900°C. The dust in the flue gas is removed by a dust remover. Next, the granular coal in the molded shape (Formed cylindrical shape of $\Phi 0.8 \times 1.2$ cm) is introduced from the top of the reactor 14, where the mold shaped coal has changed into coke by the indirect heating of the flue gas. Furthermore, the coke could be changed into activated coke by the flue gas directly in the activation reactor 13. The toxic substances such as CO, H₂ et al, from the process of making coke and activation is converted with burning in the conversion device 2, where it can be changed into non-toxic gases and come back to the system. The activated coke moves continuously from the reactor 13 to the activated coke bin 7 through the conveyors and bucket lifts to be prepared for desulfurization.

3.2. SO₂ removal and activated coke regeneration section

The activated coke moves continuously from top to bottom through the desulfurization

tower 11, where the majority of the SO₂ and air toxics adsorption occurs (or NO_x reduction with the addition of NH₃ occurs). The SO₂ toxics filled activated coke is discharged from the bottom of the tower and sent to the regeneration section by the conveyors and bucket lifts. The activated coke is indirectly heated by the flue gas or an external furnace's combustion air in the tower 12. It is called the SO₂-rich gas, which is sent to the byproduct section. The SO₂-rich gas, generated in activated coke regeneration section, contains approximately 20–25% of SO₂. It can be converted into either salable elemental sulfur (purity≥99.9%) (liquid or solid), sulfuric acid (purity≥98%), or liquid SO₂. The regenerated activated coke is filtered to remove fine dusts (activated coke fine powder generated by the abrasion plus fly ash in the flue gas caught by the activated coke) through a vibration screen, and then recycled back to the desulfurization tower. The activated coke fines can be recycled and disposed off by burning as fuel. The activated coke lost by mechanical abrasion (approximately 1.0–1.4%) while circulating in the process (called mechanical loss — depends on activated coke moving velocity and distance) and by chemical consumption of SO₂ adsorption and desorption are made up by the addition of fresh activated coke after the vibrating screen.

Especially, this process is suitable for China, where the coal accounts for 76% of the primary energy supply and there is not enough water (especially North area). It can be retrofitted or installed in new applications, and does not require pre or post-treatment reheat. In conclusion, the process is a suitable candidate for simultaneously reducing emissions of SO_x, NO_x, air toxics and volatile organics from fossil fuel and waste combustion plants.

Fig.1 The schematic of process flow of Activated coke production and desulfurization for coal fired boiler exhaust gas

4. Experimental

The reactor for the activated coke preparation and SO₂ removal activity was constructed in a fixed-bed equipment (as shown in Fig. 2) to achieve industrial purposes with three sections: the stainless steel reactor (Φ6×50cm for activated coke preparation, Φ2.5×50cm for SO₂ removal activity), the gas feeding system and the gas analyzer.

The activated coke can be prepared with this device at high temperature and the SO₂ in the exhaust gas (EG) can be adsorbed by the activated coke at low temperature.

4.1. Preparation of activated coke

Table 1 Proximate and ultimate analysis of coals

	Proximate				Ultimate					
	Moisture [%]	Ash [%]	Volatile [%]	Fixed carbon [%]	Ash [%]	Carbon [%]	Hydrogen [%]	Nitrogen [%]	Oxygen [%]	Sulfur [%]
Australia Illawara	1.19	22.17	19.22	57.42	22.44	67.46	4.17	1.30	4.27	0.36
Chinese Fenyang	4.2	10.4	29.8	55.6	10.0	79.12	4.81	1.60	3.13	1.34
Chinese Changyan	7.4	2.8	37.2	52.6	2.8	76.23	4.61	0.98	13.05	2.33
Chinese Tatong	6.0	2.9	31.9	59.2	2.9	75.3	4.8	0.9	13.7	2.40

The process flow schematic diagram of activated coke preparation was shown in Fig.3. It was mainly divided into three parts, molding, making coke and activation. Table 1 shows

the proximate and ultimate analysis of four kinds of raw materials. The coal from China and Australia was used as the precursor in the study. The raw materials were milled and sieved to obtain three different particle sizes about 105 μm (S), 710 μm (M), and 1mm(L) as matrixes, which were mixed with the additive to improve strength and were formed cylindrical shape of $\Phi 0.8 \times 1.2\text{cm}$.

Fig. 2 Experimental apparatus for activation and SO_2 removal

Fig. 3 Flow schematic diagram of preparation of activated coke

With the experimental device in Fig.2, the material was baked at room temperature~250°C for 1h, 250~600°C for 1~2h, 600~800°C for 1~2h in inert gas. A gaseous mixture with a composition similar to the EG, containing CO_2 (6~13%), O_2 (6~8%), H_2O (13%), SO_2 (1600ppm), and N_2 , flowed through the reactor bed. The coke was activated for 1~6h at 500~800°C by the EG and the activated coke was acquired. Three kinds of the EG composition, steam, carbon dioxide and oxygen, were used to activate the coke in this study as shown in Table 2. The reactor with the catalyst was heated to the desired temperature by an electric heater under a given N_2 flow. After the temperature detected by a thermocouple inserted in the calibrated capillary reached a steady state, SO_2 , O_2 , CO_2 and balance N_2 were introduced into the reactor. H_2O was introduced into the gas stream by administering N_2 through a water bath and its content was regulated through the temperature of the bath and confirmed by the amount of water consumed. The space velocity (SV) was regulated through changing the flow rates of the reactants and varied from 500 to 1500 h^{-1} .

Table 2 The components of EG

EG1	EG2	EG3
CO_2 (6%), O_2 (6%), H_2O (13%), SO_2 (1600ppm), the rest are N_2	CO_2 (13%), O_2 (8%), H_2O (13%), SO_2 (1600ppm), the rest are N_2	O_2 6%, H_2O 13%, N_2 81%

4.2. BET surface area and activity test of the activated coke

The activated coke's BET surface area and pore structure were determined by nitrogen adsorption at 77K using automatic BET surface area measurement equipment (AUTOSORB-1, Yuasa-ionics, Japan). The SO_2 removal activity of the EG were measured with the device in Fig.2. The gas contains 8% of oxygen, 13% of carbon dioxide, 13% of water, 1600ppm of sulphuric dioxide and balance nitrogen. The activated coke were milled and sieved to obtain a granular fraction of 10~24 mesh as matrixes. The space velocity was 1500 h^{-1} . The sulfur dioxide in the exhaust gas was adsorbed at 100°C. The concentrations of SO_2 in the outlet were measured through an on-line flue gas analyzer equipped with SO_2 sensors (Metrohm 761 Compact IC, Switzerland).

5. Results and discussion

We first discuss the results obtained from the flue gas activation and then those from the desulfurization.

5.1. Effects of raw materials

Four kinds of coals, Chinese Fenyang, Changyan, Datong and Australia Illawara were used

to prepare the activated coke, and to examine the effect of coals on the pore properties of the activated coke. Table 3 summarizes the preparation conditions, physical structure and chemical properties of various activated coke in this work. It should be pointed out that in this work, BET surface area, pore width and pore volume are determined with Horvath-Kawazoe (HK) method ⁽⁵⁾.

Fig.4 Effect of raw materials on Adsorption isotherm: Particle sizes of $\Phi 710\mu\text{m}$, 800°C for 1h in EG2.

Fig.5 CaO% values and BET surface area of raw materials: Particle sizes of $\Phi 710\mu\text{m}$, 800°C for 1h in EG2.

Fig.4 shows the adsorption isotherms of the activated coke obtained by flue gas activation with EG at 800°C . The particle size was about $710\mu\text{m}$. The isotherms were typical of microporous carbons. The adsorptive capacity of the activated coke generally changes with the area of coals. It can be seen from Fig.4 and Table 3 that there are large differences on specific surface area and pore volume for the five activated coals prepared from different coals. The activated coke from Chinese Fenyang/ Changyan mixing coal gave the highest specific surface area and pore volume, the next was from Chinese Changyan coal, the third was from Chinese Datong coal, and the one from Australia Illawara coal has the lowest values. However, the average pore width did not show a large difference for the EG activation series. There was the same change rule in the pore volume and BET surface area for the four activated coals. The contents of carbon and volatile component in the three Chinese coals are higher than that in the Australia Illawara coal, which may indicate that with the increase of the content of carbon and volatile component in a coal, the pore parameters were improved, as also reported in the literature ⁽⁶⁾ that SO_2 removal efficiency increased with volatile content in the raw coals. Especially, CaO% content is 0.36% in Chinese Changyan coal, which is about 4.3 times of that in Fengyang coal and 2 times of that in Illawara coal as shown in Fig.5. The Chinese Changyan coal had the highest CaO% value. The sum of the carbon, volatile and CaO content in the coal was $\text{THC}(\text{THC}=[\text{carbon}\%+\text{volatile}\%+\text{CaO}\%]\times 100)$ by definition in this work. THC values of the coal were shown in Fig 6. It is important to point out that THC value is expressed as the amount of three component sum in a coal excluding the additives. A higher THC was better for the activated coke preparation. The Chinese Changyan and Fenyang coal have high THC, the values of which were 113.79 and 109.0 respectively. The reason might lie in that the pore walls were eliminated with the removal of carbon and volatile atoms resulting in a higher pore volume and surface area at high temperature. Higher CaO content was also better for the activated coke preparation. It was indicated that the calcium in a coal may exist in the form of calcium carbonate. For this reason, the calcium carbonate would be decomposed in the coke forming process of activated coke preparation, and may produce many pores. These pores through on the activation stage could expand further again, and thus increase the pore volume as well as the BET surface area. On the other hand, Chinese Fenyang coal has cohesiveness, and it can take shape advantageously. In this study, we chose the coal mixture of Chinese Changyan and Chinese Fengyang. The activated coke was prepared by the coal mixture, which has better BET surface area (shown in Fig. 5). The mixture of the two coals may be the best one.

Additives added to the raw material were important to the activated coke preparation

process and the properties. Additives have two functions. The first is to make coke shape easier from small coal particle and to enhance the wear resistance. Next, it may help to increase the activated coke's surface area and pore volume to enhance the adsorptive capacity of the activated coke. In this study, the main additive is about 20~30% of the coal tar from high temperature distillation of a coal. The additives added to the raw material may also improve the THC. The result is shown in Table 4. The BET surface area increases from 25.8 to 49.45m²/g when the THC increases from 86.86 to 106.86 with loading 20~30% of coal tar.

Table 3 Characteristics of the activated coke

Sample	Raw material	Particle sizes (μm)	Yield (%)	Activation method	condition	BET surface area (m ² /g)	HK method Pore width (Å)	HK method pore volume (cm ³ /g)
I-01-L-A0	Illqware	1000	89.7	EG2	800°C, 1h	25.8	15.56	0.0263
I-02-L	Illqware	1000	86.5	EG2	800°C, 1h	49.45	14.33	0.02505
M-01-L	Mixing coal [#]	1000	85.6	EG1	800°C, 1h	50.32	13.83	0.02506
I-03-M	Illqware	710	87.4	EG2	800°C, 1h	28.5	15.0	0.0213
FY-01-M	Fenyang	710	82.7	EG2	800°C, 1h	68.1	14.02	0.036
CY-01-M	Changyan	710	81.4	EG2	800°C, 1h	79.5	14.33	0.04
DT-01-M	Datong	710	80.5	EG2	800°C, 1h	70.3	14.15	0.038
M-01-M	Mixing coal	710	82.8	EG2	800°C, 1h	110.9	14.27	0.0558
M-02-M	Mixing coal	710	82.9	EG1	800°C, 1h	110.9	13.43	0.0582
M-01-S	Mixing coal	105	74.8	EG1	800°C, 1h	417.6	12.48	0.2197
M-02-S	Mixing coal	105	62.1	EG2	800°C, 1h	540.5	13.88	0.2503
M-03-S	Mixing coal	105	75.0	EG3	800°C, 1h	403.0	12.08	0.1965
M-04-S	Mixing coal	105	89.2	EG1	500°C, 1h	62.3	14.58	0.0304
M-05-S	Mixing coal	105	79.7	EG1	600°C, 1h	245.1	14.12	0.1274
M-06-S	Mixing coal	105	76.0	EG1	700°C, 1h	365.3	14.58	0.1864
M-07-S	Mixing coal	105	55.45	EG1	800°C, 2h	399.3	12.27	0.215
M-08-S	Mixing coal	105	53.9	EG1	800°C, 3h	459.4	12.27	0.2197
M-09-S	Mixing coal	105	26.9	EG1	800°C, 5h	451.8	12.17	0.2243
M-S00-S	Mixing coal	105	88.8	10% H ₂ O	800°C, 1h	401.0	13.99	0.2010
M-S01-S	Mixing coal	105	85.0	30% H ₂ O	800°C, 1h	455.4	14.15	0.2503
M-S02-S	Mixing coal	105	82.3	40% H ₂ O	800°C, 1h	501.2	13.13	0.2516
M-S03-S	Mixing coal	105	80.0	50% H ₂ O	800°C, 1h	546.7	12.12	0.2575
M-S04-S	Mixing coal	105	80.3	60% H ₂ O	800°C, 1h	547.0	12.23	0.2585
M-S05-S	Mixing coal	105	80.1	70% H ₂ O	800°C, 1h	552.3	13.01	0.2655
M-C01-S	Mixing coal	105	88.5	5% CO ₂	800°C, 1h	302.1	14.57	0.1867
M-C02-S	Mixing coal	105	86.1	15% CO ₂	800°C, 1h	379.3	14.12	0.1898
M-C03-S	Mixing coal	105	84.2	20% CO ₂	800°C, 1h	380.2	13.98	0.1923
M-C04-S	Mixing coal	105	83.0	30% CO ₂	800°C, 1h	390.7	13.88	0.1933
M-C05-S	Mixing coal	105	83.6	40% CO ₂	800°C, 1h	398.6	13.67	0.1997
M-C06-S	Mixing coal	105	82.5	50% CO ₂	800°C, 1h	400.0	13.87	0.2032

[#]Mixing coal that was mixed with 25%Chinese Fenyang coal and 75%Chinese Chang yang coal.

Fig.6 THC values of raw materials: Particle sizes of Φ710μm, 800°C for 1h in EG2,

Table 4 Effect of the additive

sample	I-01-L-A0	I-02-L
additive	No any	20.0 wt.% coal tar
THC(including additive)	86.86	106.86

Table 5 The relativity rate of activation reaction

Reaction	Relativity rate
C+H ₂ O	3
C+CO ₂	1
C+O ₂	1×10 ⁵
C+H ₂	3×10 ⁻³

Paolo Davini ⁽⁷⁾, Jianrong Ma et al ⁽²⁾, Yanli Wang et al ⁽⁸⁾, used the metal salt and the oxide compound in activated coke may sharpen the desulphurization ability. The metal salt and the oxide compound have the catalytic effect for SO₂ transformation. Therefore, it can enhance the desulphurization ability of the activated coke. Alkali and alkaline-earth metal oxides in the binder were proposed to be the main factors affecting the activities of SO₂ removal. The work of loading CaCO₃ on activated coke will be discussed in next thesis.

5.2. Effect of the coal particle size

Fig.7~8 shows the effect of different coal particle sizes. The particle sizes of coal used were about Φ1mm (L), Φ710μm (M) and Φ105μm (S). Three kinds of coal sample formed in cylindrical shape were subject to pyrolysis in the vertical reactor prior to activation,

which was activated by EG1 at 800°C. It can be seen in Fig.7 that the large particle size coal always exhibit a higher yield compared with those from the activated coke regardless of BET surface area. The one made from $\Phi 105\mu\text{m}$ raw material shows the highest BET surface area and the lowest yield. Therefore, for smaller particle size, weight loss is higher and surface area as well as micropore volume is more improved. A. Ahmardpour et al.⁽⁴⁾ in studying the effect of chemical agent on coal by chemical and physical activation with carbon dioxide also found that small particles show better activation. In Fig.8 the micropore

Fig.7 Effect of raw material size on yield and BET surface area: 800°C for 1h in EG1, Mixing coal

Fig.8 Effect of raw material size on pore distributions: 800°C for 1h in EG1, Mixing coal

volumes deduced from the HK method using N_2 adsorption isotherm data at 77K are also compared. When the particle sizes of coal changed from $\Phi 1\text{mm}$ to $\Phi 105\mu\text{m}$, the BET surface area increased 8.3 times, and the cumulative pore volume increased from 0.02506 to 0.2197 cm^3/g . It is about 8.8 times. The smaller coal size is beneficial to the formation of the larger pore coal may be due to differences in ingredients which led to the ability to absorb the difference.

5.3. Effects of activation temperature

The effect of the activation temperature on the properties of the activated coke prepared was studied using $\Phi 105\mu\text{m}$ coal mixture and the result is shown in Figs. 9 and 10. When the temperature changed from 500 to 800°C, the pore volume had a very big change and the

Fig.9 Effect of activation temperature on pore size distributions: Reaction time of 1h in EG1, particle sizes of $\Phi 105\mu\text{m}$, Mixing coal.

Fig.10 Effect of activation temperature on BET surface area and yield: Reaction time of 1h in EG1, particle sizes of $\Phi 105\mu\text{m}$, Mixing coal.

average pore width only has small changed at about below 700°C. The average pore width of the activated coke from HK method is 12.48Å at 800°C, and the cumulative pore volume is 0.2197 cm^3/g . The pore volume increases about 17.9% and the average pore width decreases about 14.4% from 700 to 800°C. However, the pore volume increases about 85.5% and the average pore width decreases 14.4% from 500 to 800°C. In other words, the temperature was very important in the activated coke preparation process, It influenced the absorbing ability of the activated coke directly. The BET surface area change shown in Fig .10 has proved this too. The BET surface area quickly increases from 62.3 to 418 m^2/g with increasing temperature from 500 to 800°C, and the yield only slightly decreases. So, it is reasonable to choose 800°C according to the temperature of the exhaust gas of the coal

power plant. It was suitable for the carbon reaction with the EG at 800°C.

5.4. Effects of the activating agents

Five typical activating gases were employed to examine the effects of activating components. The experimental results are shown in Fig.11 and Fig.12.

The coke was prepared by the coal with Chinese Fenyang/Changyan mixing coals. The carbonization was conducted at 600~800°C for 2 hours, and then was activated at 800°C for 1h. The particle size was about 105µm. Fig.11 shows the isotherms of the activation with the five activating gases at 800°C. The adsorptive capacity of the activated coke has generally changed with different activating gases. It can be also seen from Fig.12, which was calculated with HK method, that there was a different pore volume, but the same

Fig.11 Effect of activating agents on adsorption isotherms of the activated cokes: Particle sizes of $\Phi 105\mu\text{m}$, 800°C for 1h.

Fig.12 Effect of activating agents on pore size distribution of HK method: Particle sizes of $\Phi 105\mu\text{m}$, 800°C for 1h.

microporous width for the different activating gases. The high porosity and the pore volume of the activated coke can be obtained by the steam and EG2 activation.

It is considered that EG activation is both a physical and a chemical process^{(1), (4)}. The reaction principle of the gases activation is as follows:

1. The steam activation

The steam activation is the most commonly used method. When the steam got into the reactor at high temperature, initially, there was a different surface tension between the coal and the steam. The coal surface pore width can change into a larger one resulting from the vapor function. The treatment process was usually considered as a physical activation. In the second place, H_2 , CO and CO_2 were produced by the steam and carbon due to chemical reaction, leading to the pore of the coke unceasingly rich from the surface to inside. Thus, the pore volume and surface area of coke was increased. The reaction mechanism might be as follows.

In other words, the carbon surface and the steam have been combined to emit the hydrogen and carbon monoxide, and the hydrogen in carbon surface restrained the reaction, $\text{C} + \text{H}_2 \leftrightarrow \text{C} [\text{H}_2]$. Produced carbon monoxide reacted with oxygen and water to form carbon dioxide. $\text{CO} + \text{C} [\text{O}] \rightarrow \text{C} + \text{CO}_2$, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 + 9.6 \text{ kcal}$.

J. P. Blakely and L. G. Overholser⁽⁹⁾ considered this as approximate the first step reaction. The reaction is as follows:

$$r = \frac{24.1y_{\text{H}_2\text{O}}P_r}{1 + 0.20y_{\text{H}_2}P_r + 0.0097y_{\text{H}_2\text{O}}P_r} \quad (1)$$

where r is the reaction rate (%/hr), P_r is the system pressure. Because the y_{H_2} was very low in the experiment, it can be regarded as zero. The Eq. (1) may be described by Eq.(2) :

$$r = \frac{k_1y_{\text{H}_2\text{O}}P_r}{1 + k_2y_{\text{H}_2\text{O}}P_r} \quad (2) \quad r = \frac{145.3y_{\text{H}_2\text{O}}P_r}{1 + 5.7y_{\text{H}_2\text{O}}P_r} \quad (3)$$

The reaction rate Eq.(3) can be obtained with the steam activation experiment data (Table 3)

and the model Eq. (2) by computer curve fitting.

Fig. 13 shows the reaction rate of experiment and calculation on H₂O% concentration varied during the activated coke preparation process. The BET surface area increases from 455.4 to 546.7m²/g with increasing water concentration from 30% to 50%. With further increase of H₂O%, the BET surface area hardly does not change. The reaction rate (1-r) slightly decreases from 85 to 80.1%, and the experimental value is the same as that predicted by Eq. (3). The results indicated that the reaction rate of steam activation could be calculated by Eq. (3). It is considered that is approximate the first step reaction.

2. The CO₂ activation

This reaction was slower than the steam reaction. The reaction mechanism might be as follows: $C + CO_2 \rightarrow C[O] + CO$, $C[O] \rightarrow CO$, $C + CO \leftrightarrow C[CO]$

The reaction was possibly hindered due to the CO produced in the process. For instance, J. R. Arthur et al ⁽¹⁰⁾ reported that its relations can be showed as follows:

$$CO/CO_2 = 10^{3.4} e^{-12400/Rg} \quad (4)$$

$$r = \frac{k_1 y_{CO_2} P_r}{1 + k_2 y_{CO} P_r + k_3 y_{CO_2} P_r} \quad (5)$$

Fig.13 The yield of the steam activation reaction:
Particle sizes of $\Phi 105\mu m$ mixing coal, 800°C for 1h

Fig.14 The yield of the carbon dioxide activation reaction:
Particle sizes of $\Phi 105\mu m$ mixing coal, 800°C for 1h

Because of the temperature is 800°C, the value of y_{CO} in system is $3.24y_{CO_2}$ by Eq. (4). Then the reaction rate Eq.(6) may be given by Eqs.(4) and (5).

$$r = \frac{k_1 y_{CO_2} P_r}{1 + (3.24k_2 + k_3) y_{CO_2} P_r} \quad (6)$$

$$r = \frac{479.3 y_{CO_2} P_r}{1 + 25.8 y_{CO_2} P_r} \quad (7)$$

We can express the reaction rate of CO₂ using model Eq. (6) and the CO₂ activation experiment data (Table 3) as Eq.(7). The coefficient of Eq.(7) are given by computer curve fitting. The results of the experiment and the reaction rate from calculation with different concentration CO₂ are shown in Fig 14. The BET surface area increases from 302 to 380m²/g with increasing CO₂ concentration from 5% to 20%. The reaction rate also slightly changes between 88.5% and 84.2%. Further increasing CO₂%, the BET surface area nearly does not change. It is considered that is approximate first step reaction too. These results suggest that the CO₂% be lower than 20%.The content of CO₂% could be controlled in the range 10~20%.

3. The O₂ activation

This is an exothermic chemical reaction and it can generate higher reaction heat in the process. Fig.15 shows the effect of thermogravimetry analysis (TGA) with different concentrations of oxygen. The initial reaction temperature is about 300°C at an O₂ content of 21%, and that is above 450°C at low oxygen concentration (below 6% of O₂). The reaction rate of C+O₂ is the fastest at high temperature. The effect of O₂ content on the coke activity was studied using M-03-S and the result of BET surface area and yield is 403m²/g and 75% respectively at an O₂ content of 6%. Therefore, The oxygen in EG cannot too be high. Generally it was lower than 10%. If not, it is disadvantageous to the activated coke

production.

Fig.15 The curve of thermogravimetry analysis on oxygen activation

step because it contains CO₂, CO, H₂O and O₂ in the flue gas. The experimental results indicate that the steam is a good activating agent for the activation of coke to activated coke, which also certifies that steam was usually used in activated coke and activated carbon production. The experimental results also indicated that the flue gas activation lead to good results on BET surface area and pore volume. The BET surface area and pore volume reached 540.5m²/g and 0.2503cm³/g (M-02-S), respectively, with EG2 activation, which are the same as that with the steam activation.

5.5. Effects of activation time

The effects of the activation time on the pore structure of the activated coke were

Fig.16 Effect of different activation time: Reaction temperature of 800°C in EG1, particle sizes of $\Phi 105\mu\text{m}$, Mixing coal.

Fig.17 Effect of different activation time on adsorption isotherms of the activated cokes: Reaction temperature of 800°C in EG1, particle sizes of $\Phi 105\mu\text{m}$, Mixing coal.

explored. The activated coke was prepared from Chinese Fenyang/Changyan coal mixture with EG1 activation at 800°C. The particle size was about 105 μm . The results are shown in Fig.16, and the adsorption isotherms of the activated cokes are shown in Fig.17. The BET surface area slightly increases from 417.6 (m²/g) to 451.8(m²/g) with increasing activation time from 1 to 5 hour. However, the yield changes from 74.8% to 26.9%. The decrease is faster that dropped nearly 50%.The pore volumes increase from 0.2197 to 0.2243 (cm³/g), the pore width decrease from 12.48 to 12.17 Å. There is only a slight change.

While maintaining a constant chemical ratio, Fig.16 shows that the surface area and the chemical ratio of the activation increase with the time for carbonization at 800°C. The increase indicates that prolonged heat treatment is required for the full development of porosity at 800°C. The development of porosity is also accompanied by a narrowing of the porosity since the average pore width is the smallest for the carbonization of 5 hours. It can be seen that the microspore volume generally increases with the carbonization time. Since the coke structure has already been well developed at this temperature, the increase with activation time simply causes the break of the cross-links between carbon structures, with a consequent collapse of pores. Obviously, the activation time affects porosity and yield of the activated coke, it was important to the activated coke prepared. In view of practical applications, if it is decided that the temperature of activated coke activation is 800°C, then the appropriate activation time should be about 1 hour to ensure the operation of the coke

activation.

5.6. Properties of SO₂ adsorption

The contrast experiment was made for the SO₂ absorption by two groups of activated coke. The laboratory prepared the columnar activated coke by EG activated at 800°C with a diameter of 0.8cm, a height of approximately 1.2cm and a BET surface area of 418m²/g. Japan MMC produces the almond shaped activated coke by steam activation with a

Fig.18 Desulfurization activity of the activated coke: Temperature of 100°C, space velocity 1500h⁻¹, the exhaust gas content of EG2

The SO₂ desulfurization in the prepared activated coke (EG activation) and the commercial activated coke (steam activation) experiment were compared in Fig.18. it can be seen that the SO₂ conversion curves with EG activation (M-01-S) are similar to that of steam activation line. Experiment results also showed that the SO₂ adsorption capacity of the activated coke from the EG activated at 800°C was approximately the same as the steam activated one. The SO₂ adsorption capacity of the activated coke is above 100mg-SO₂/g-activated coke. But, both M-01-L and I-02-L have almost the same BET surface area, they also have different SO₂ capture capacities. It may be due to the difference in raw material ingredients resulting in the absorptive ability difference. For example, the value of THC was 110.33 for M-01-L and 86.86 for I-02-L. The amount of SO₂ captured was 42 and 28mg-SO₂/g-activated coke respectively. It is important to point out that sulfur retention is expressed as the amount of SO₂ captured (by weight) per 1g activated coke before SO₂ conversion decreases to 50%. The following mechanism for SO₂ removal by activated coke may explain the results presented here Table 6⁽¹¹⁾:

Table 6 The mechanism of SO₂ removal by activated coke

Oxygen chemisorption	$C + 1/2O_2 \rightarrow C-O \text{ or } C(O)$	H ₂ SO ₄ formation	$C-SO_3 + H_2O \rightarrow C-H_2SO_4$
Fleeting complex	$C-O \rightarrow C(O)$	Regeneration	$C-H_2SO_4 \rightarrow C + H_2SO_4$
SO ₂ adsorption	$C(O) + SO_2 \rightarrow C-SO_3$	Overall reaction	$C + SO_2 + 1/2O_2 + H_2O \rightarrow C + H_2SO_4$

This mechanism implies that the pore volume of the activated coke, i.e. the amount of water retained in the pores, determines the total amount of SO₂ adsorbed by the carbon. Hartman and Coughlin⁽¹²⁾ found the catalytic oxidation of SO₂ to SO₃ by carbon to be the rate-determining step (in the absence of diffusional limitations) in the conversion of SO₂ to H₂SO₄. If the rate-determining step is indeed catalytic oxidation of SO₂ to SO₃, the rate of SO₂ adsorption could be expressed as $\frac{d[SO_2]}{dt} = k[C(O)][SO_2]^n$ (8)

Where k is a fundamental rate constant (turnover frequency of the carbon catalyst) and n is the order of the reaction. Anthony A. Lizzio and Joseph A. DeBarr⁽¹¹⁾ found the kinetics of SO₂ adsorption on commercial activated coke at various concentrations of SO₂ ranging from 100 to 3000ppm. It can be inferred that for these reaction conditions of SO₂>1500ppm, the reaction order lies between zero and one, and for concentrations of SO₂>1500ppm, the reaction order approaches zero. It is important to note that adsorption equilibrium is not reached even after 40h. This suggests that under these conditions the H₂O adsorbed in the pores has yet to be saturated with H₂SO₄. The reaction at the catalyst surface between C(O) and SO₂ proceeds until an equilibrium is established between the H₂SO₄ adsorbed water. At equilibrium, the pore volume of the activated coke determines its

SO₂ adsorption capacity.

6. Conclusion

Flue gas from the power plant was proposed as the activating agent in the preparation of activated coke. The types of coal, activating agents, activation temperature, and activation time have large influence on the pore parameter and the properties of SO₂ removal.

1. Raw material is very important to the activated coke preparation and SO₂ removal activity. Among the THC value investigated, the coal with a smaller coal size and a higher coal THC is the optimal raw material for the desulfurizer.

2. The O₂, CO₂ and H₂O can all be used for coke activation. The content of suitable oxygen is lower than 10%, and the content of CO₂ is between 10% and 20% in flue gas. Then, a higher concentration of water is conducive to the activation.

3. The activated coke (M-02-S) showing the best BET surface area in this EG activation study is 540.5m²/g from mixing coal and prepared as follows: 105μm small size mixing coal with coal tar (20~30%), baked at 800°C, activated at 800°C with EG2 for about 1h.

4. The operating conditions are temperature 100 °C, SO₂ content 1600ppm and space velocity 1500h⁻¹, at which SO₂ absorptive capacity reaches above 100mg-SO₂/g-activated coke. The activated coke with EG activation had almost the same SO₂ adsorption capacity as that with steam activation.

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