Mechanism of SO_2 adsorption and desorption on commercial activated coke

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Abstract−We used commercial activated coke (AC) as adsorbent and fixed-bed, FTIR, N_2 adsorption, ion chromatograph as research methods to study the SO_2 removal mechanism in the presence of O_2 and H_2O and adsorbate (H_2SO_4) desorption mechanism by combined regeneration. The results showed that AC saturation sulfur retention (52.6 mg/g) in $SO_2+O_2+H_2O$ atmosphere was 4.6 times as much as that (11.4 mg/g) in SO_2+O_2 atmosphere and 5.0 times as much as that (10.6 mg/g) in SO_2+O_2 atmosphere at 90 °C. O_2 and H_2O were necessary in AC desulfurization process. Reaction of SO_3 and H_2O (g) and condensation of sulfuric acid vapor were the dynamic of AC desulfurization process. Water vapor blowing in combined regeneration inhibited the reaction between H_2SO_4 and carbon, and consequently reduced the chemical lost of carbon. AC cumulative quality loss (53.6%) of five-times in C-R was still less than that (62.4%) of three-times in H-R. Water vapor blowing inhibited reactivation effect, as a result reducing the changes of AC pore structure and surface functional groups. Adsorbate H_2SO_4 generated in desulfurization evaporated to sulfuric acid vapor due to the high temperature in regeneration and was carried out by water vapor.

Key words: Activated Coke, SO_2 Removal, Desorption, Combined Regeneration, Carbon Loss

INTRODUCTION

Coal is a major resource in China [1]. Sulfur dioxide (SO_2) emission from coal combustion is one of the major anthropogenic contributors to air pollution [2]. Activated coke (AC), made by coal, is a kind of carbonaceous material. Applying AC for flue gas desulfurization, which has the advantages of water-saving and pollutant recyclable utilization, is considered an important development direction of SO_2 removal [3,4]. Domestic and foreign researchers have done a great deal of work on SO_2 adsorption by AC. For AC desulfurization behavior, it is generally considered [5-8] that SO_2 is adsorbed onto the surface of carbonaceous material and converted to SO_3 by oxidation with O_2; then with the effect of hydration and elution, it exists as sulfuric acid. However, different researchers have not reached a uniform conclusion on the effect mechanism of O_2 and H_2O on SO_2 removal process. Raymundo-Pinero, Rubio et al. [9,10] found that when O_2 was present, adsorbed SO_2 reacted with oxygen on AC to form adsorbed SO_3. But these scholars did not give conclusive evidence of the existence of SO_3 in the presence of O_2. As for the effect of H_2O, following the mechanism of some scholars (Mochida [6], Gaur [11], Zhang [12], Lizzio [13] et al.), H_2O is postulated to have dual roles: one is to react with the adsorbed SO_3 to form adsorbed H_2SO_4 (hydration), and the other is to dissolve the adsorbed H_2SO_4 from the surface (elution). However, some authors [14-16] have proposed different views: the role of H_2O is not only reacting with SO_3. More importantly, H_2O provides a proton (H^+) which participated in the oxidation reaction of SO_2. Above analysis shows that the mechanism of SO_2 removal in presence of O_2 and H_2O needs further research.

After desulfurization process, adsorbate H_2SO_4 has to be removed from AC interior to recover the adsorption ability of AC. Traditional AC regeneration methods mainly include heating regeneration and water scrubbing regeneration [17]. Mochida analyzed the mechanism of heating regeneration and water scrubbing regeneration. According to the analysis of Mochida, water scrubbing requires large amounts of water since H_2SO_4, produced in the pores of AC, must be extracted. Furthermore, strongly adsorbed H_2SO_4 tends to remain and be hard to regenerate completely. In heating regeneration, H_2SO_4 was dehydrated and reduced to SO_2 by reacting with carbon. Carbon loss is not negligible. Feng [18] and Fei [19] have studied the AC regenerative property of different methods. Following their results, a certain degree of quality loss of AC took place in heating regeneration. The cost of AC adsorbent is the key issue to commercialize the heating regeneration technology. Improvement of existing regeneration methods or new regeneration methods investigation is significant to the large-scale application of AC desulfurization technology.

The first objective of this paper was to study the SO_2 removal mechanism in the presence of O_2 and H_2O and obtain SO_2 conversion and existence form in AC pores by using commercial AC as adsorbent. On the basis, ACs after desulfurization were used to be regenerated. The highlight of our research is that we have proposed a new regeneration method which combines the advantages of both heating regeneration and water scrubbing regeneration, adding water vapor blowing in heating regeneration process, called combined regeneration. The effect of water vapor and mechanism of new regeneration method are revealed.

EXPERIMENTAL SECTION

1. Sample Preparation

The sample used in this paper was bought from Inner Mongolia Alashan Kexing Carbon Industry Co., Ltd. Proximate and elemen-

Table 1. Proximate and ultimate analysis of AC

Proximate analysis/%		Ultimate analysis/%	
M_{ad}	0.2	C_{ad}	87.520
V_{ad}	2.4	H_{ad}	0.905
A_{ad}	11.9	N_{ad}	0.600
FC_{ad}	85.5	S_{ad}	0.285
		O_{ad}	10.690

tal analysis results of activated coke (AC) are shown in Table 1.

2. Desulfurization and Regeneration Property Evaluation of AC

SO_2 removal and regeneration tests were carried out with fixed-bed equipment as illustrated in Fig. 1. The reactor (inner diameter 13 mm) was made of glass and sand core. In a typical run, 5 g of samples was loaded into the reactor. Temperature was controlled by a vertical tube furnace whose temperature fluctuation was under 1 K. In SO_2 removal test process, the reactor with AC was heated to the desired temperature; subsequently required gas was introduced into the reactor after the temperature detected by a thermocouple inserted in the reaction zone reached a steady state. Portable FTIR of Finland Gasmet Company was used to online monitor SO_2 concentration of reactor inlet and outlet. The test lasted until SO_2 concentration remained constant and reached adsorption saturation. The sulfur content of samples before and after adsorption was determined by 5E-IRSII Infrared sulfur meter of Changsha Kaiyuan

Instruments Co., Ltd. SO_2 removal property of samples were characterized through SO_2 removal efficiency and saturation sulfur retention.

SO_2 removal efficiency is defined as:

$$DeSO_2\ (\%)=[SO_2\ (in)-SO_2\ (out)/SO_2\ (in)]\cdot 100 \qquad (1)$$

In the formula, SO_2 (in) and SO_2 (out) are inlet SO_2 concentration and outlet SO_2 concentration measured by FTIR.

Saturation sulfur retention of samples was calculated as:

$$h\ (mg/g)=2000\ (MK\text{-}mk)/m \qquad (2)$$

In the formula, m is the sample weight before adsorption (g); M is the sample weight after adsorption (g); K is sulfur content of sample after adsorption (%); k is sulfur content of sample before adsorption (%); 2000 is a coefficient of conversion for g to mg and S to SO_2.

Simulated flue gas composition and test conditions are given in Table 2.

In AC regeneration test, we turned off the pressure reducing valves of SO_2 and O_2, and subsequently heated the tube furnace to the required temperature. Then, N_2 or the mixture of N_2 and water vapor (flow rate 0.5 L/min; N_2 and water vapor volume ratio 4 : 1) was introduced into the reactor which was filled with adsorption saturated AC to achieve heating regeneration or combined regeneration. Water scrubbing regeneration test conditions were as follows: we loaded the AC after desulfurization into a 250 mL beaker with 150 mL distilled water, and subsequently stirred suspension liquid and
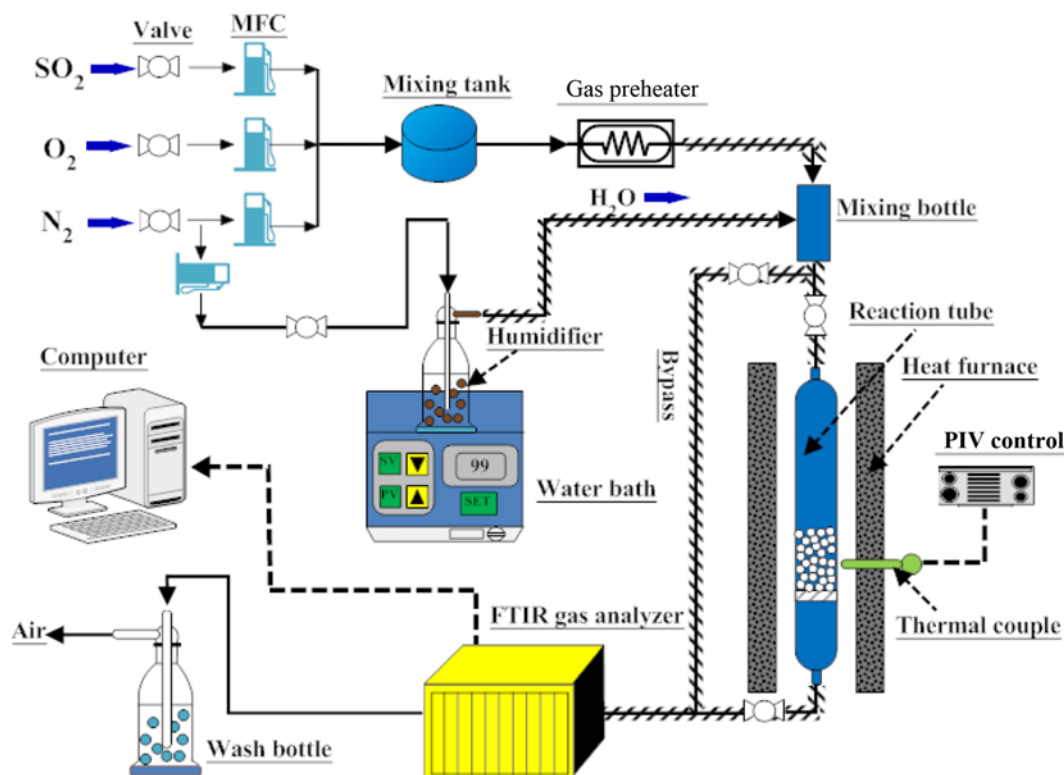

Fig. 1. Scheme of desulfurization and regeneration equipment: The fixed-bed reactor was the main body of experiment system. The names of relevant experimental equipment were marked in the figure. The water vapor needed in desulfurization and regeneration process was carried by nitrogen from the water bath.

(a) SO_2 removal efficiency varies with time in SO_2 atmosphere, (b) So_2 removal efficiency varies with time in SO_2+O_2 atmosphere

Table 2. SO$_2$ removal conditions and simulated flue gas composition

Experimental conditions		Simulated flue gas composition	
Partical diameter (mu)	20-30	SO$_2$ (%)	0-0.3
Gas velocity (m/s)	0.2	O$_2$ (%)	0-10
Gas flow (L/min)	1.592	H$_2$O (%)	0-16
Temperature (K)	303-393	N$_2$	Balance

replaced the water every 10 minutes. Regeneration time of all methods was set at 30 minutes. Quality loss (θ) of ACs in regeneration process, which is defined as the ratio of reduced quality to non-regenerative quality, was analyzed to characterize the loss degree of different methods. SO$_2$ removal activity of regenerative ACs was evaluated in the above-mentioned fix-bed equipment.

3. Characterization of ACs

Porous characteristics of ACs were determined with N$_2$ ($-196\,^{\circ}$C) adsorption isotherms by using ASAP2020 apparatus (Micromeritics Instrument Corporation) for nitrogen adsorption. Surface area was measured by BET method. Micropore volumes were calculated by t-plot method. Mesopore volumes were determined with BJH pattern. NaOH solution was used to immerse ACs after desulfurization and absorb regeneration products. Subsequently, IC-3000 Ion chromatograph (American Dionex Corporation) was used to detect SO$_3^{2-}$ and SO$_4^{2-}$ contents in the absorption solution. The aim was to obtain the form of sulfur conversion and desorption in removal and regeneration process. Ion composition of tested solution was analyzed through the contrast of tested solution chromatogram and standard solution chromatogram. The surface functional groups on the ACs surface of original ACs and regenerative ACs were determined by FTIR with a resolution of 2 cm^{-1} and 40 scans to analyze the types of functional groups changing in the regeneration process.

RESULTS AND DISCUSSION

1. SO$_2$ Removal Mechanism in Presence of O$_2$ and H$_2$O

1-1. Effect of O$_2$ on SO$_2$ Conversion Process

During AC desulfurization process, O$_2$ is necessary, but its effect mechanisms from different researchers are various. Raymundo-Pinero, Rubio et al. [9,10] have found that when O$_2$ was present, adsorbed SO$_2$ reacted with oxygen on activated coke to form adsorbed SO$_3$, and it was the reason why AC's sulfur capacity increased. But some scholars also found that activated carbon materials cannot oxidize SO$_2$ to form SO$_3$ without H$_2$O; SO$_2$ can show reducibility only in presence of H$_2$O and it is difficult for SO$_2$ to react with O$_2$ under completely dry conditions. Therefore, SO$_2$ adsorption and SO$_2$+O$_2$ adsorption of AC under different temperatures are firstly studied. Fig. 2(a) and Fig. 2(b) are AC adsorption curves in SO$_2$ and SO$_2$+O$_2$ atmospheres, respectively. As can be seen from Fig. 2(a), AC saturation adsorption time gradually decreases with temperature increasing. Saturation adsorption time at 30 $^{\circ}$C is 37 minutes while saturation adsorption time at 120 $^{\circ}$C is just 12 minutes. When temperature increases, the adsorption curve moves inward and adsorption capacity of AC declines rapidly. As we know, the typical characteristic of physical adsorption is similar to condensation and it is an exothermic reaction. With temperature increasing, the amount
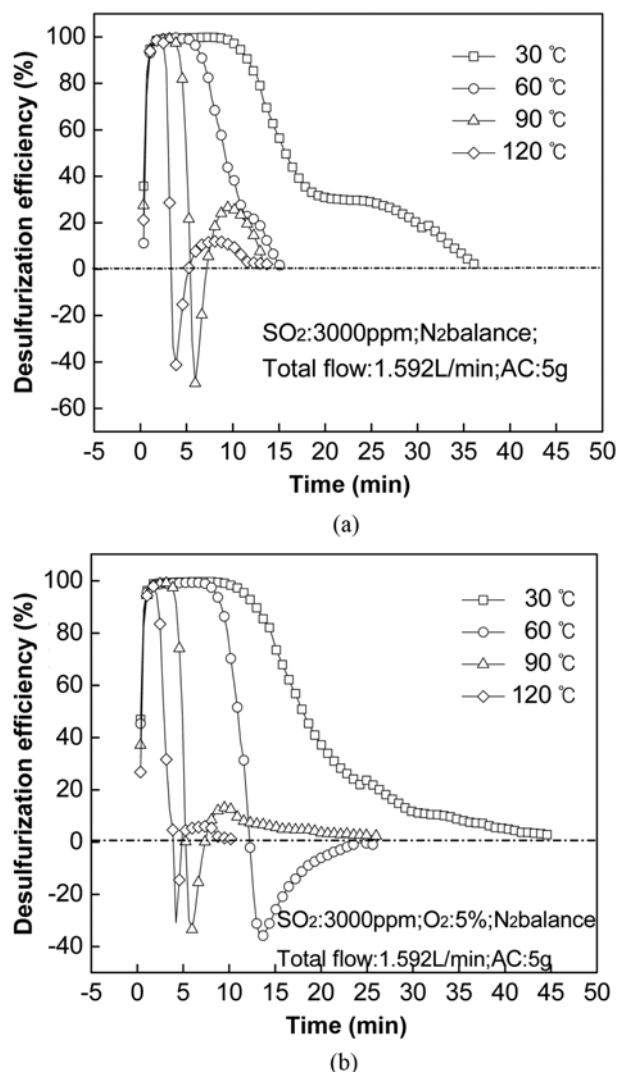

(a)

(b)

Fig. 2. SO$_2$ removal efficiency varies with time in SO$_2$ and SO$_2$+O$_2$ atmosphere: the curves of figure (a) was obtained in SO$_2$ atmosphere, to get physical adsorption property of AC; the curves of figure (b) was obtained in SO$_2$+O$_2$ atmosphere, to get the effect of O$_2$ on SO$_2$ adsorption property of AC.

of physical adsorption decreases rapidly. Related researchers [12.15] considered that SO$_2$ adsorption of AC without O$_2$ and H$_2$O is a physical adsorption process. The results also prove the conclusion. Fig. 2(b) shows that AC adsorption capacity in presence of O$_2$ is similar to that of SO$_2$ atmosphere. However, at the same adsorption temperature, we can see that AC saturation adsorption time in presence of O$_2$ is more than that of SO$_2$ alone. Saturation sulfur retention under two kinds of adsorption conditions at 30 $^{\circ}$C was calculated in the test. AC saturation sulfur retention (37 mg/g) in SO$_2$+O$_2$ atmosphere is 1.3 times as much as that (28.3 mg/g) in SO$_2$ atmosphere. This indicates that SO$_2$ adsorption capacity of AC improves in the presence of O$_2$. To further understand the role of O$_2$ in SO$_2$ adsorption process, AC after adsorption was immersed in NaOH solution and ion chromatograph was used to analyze SO$_3^{2-}$ and SO$_4^{2-}$ in our test. It is observed that not only SO$_3^{2-}$ but also SO$_4^{2-}$ exists in the AC immersing solution in SO$_2$+O$_2$ atmosphere. This shows that the presence of O$_2$ promotes the formation of S^{6+} in the AC adsorption process.

In the absence of H_2O, S^{6+} must exist in the form of SO_3. Combining our test results and related scholars' conclusion [6-10], it is considered that O_2 makes some chemical adsorbed SO_2 be oxidized to SO_3 whose adsorption pattern is different from that of SO_2. The reaction makes SO_2 adsorption active sites vacant and creates the conditions to further adsorb SO_2.

From Fig. 2(a) and (b), we can see negative values of SO_2 removal efficiency. According to equilibrium theory, adsorption and desorption occur simultaneously in the AC adsorption process. SO_2 adsorption capacity is decided by both adsorption and desorption rate. From our result and relevant scholars' research [6-10], in SO_2 and SO_2+O_2 adsorption process, physical adsorption is the main step. As we know, the interaction force (van der Waals force) between adsorbate and adsorbent is relatively weak in physical adsorption. Therefore, molecular kinetic energy of adsorptive SO_2 on AC improves when adsorption temperature increases. As a result, SO_2 can overcome intermolecular force and desorb from AC surface. When temperature is high, the rate of desorption is great. As we know, multilayer adsorption is the main characteristic of physical adsorption, so we can deduce SO_2 is adsorbed in the form of multilayer adsorption. When the temperature is relatively high (60 °C, 90 °C, 120 °C in our test), the desorption rate can exceed the adsorption rate and adsorbate SO_2 in the form of multilayer adsorption will desorb like an avalanche. As a result, we can see that, with adsorption proceeding, negative values of desulfurization efficiency can be found at a time in our test.

It has been revealed by Mochida [6], Lizzio [13], Zhang [15] et al., that SO_2 adsorption capacity of AC increases dramatically in the presence of O_2 and H_2O. To obtain the effect mechanism of O_2 in $SO_2+O_2+H_2O$ atmosphere, AC adsorption capacity in the presence or absence of O_2 is studied. The results are shown in Fig. 3. In the process of A-B, SO_2 adsorption behavior of AC in SO_2+H_2O atmosphere is similar to that in SO_2 alone. The presence of H_2O does not increase SO_2 adsorption capacity. This shows that even in AC interior, there is still almost no reaction between SO_2 and H_2O. After B point, the adding of O_2 makes SO_2 adsorption property in-
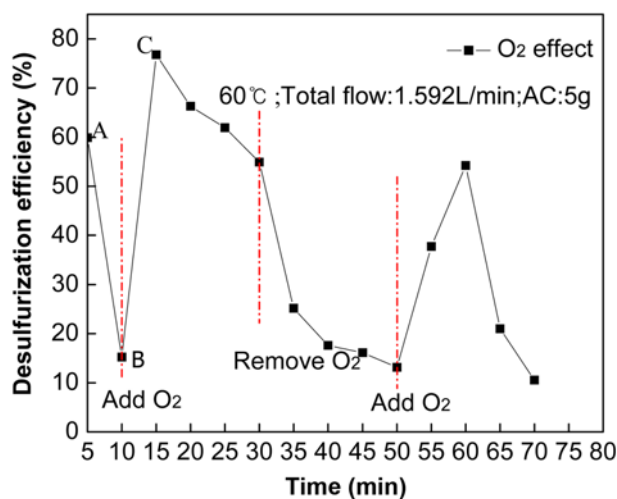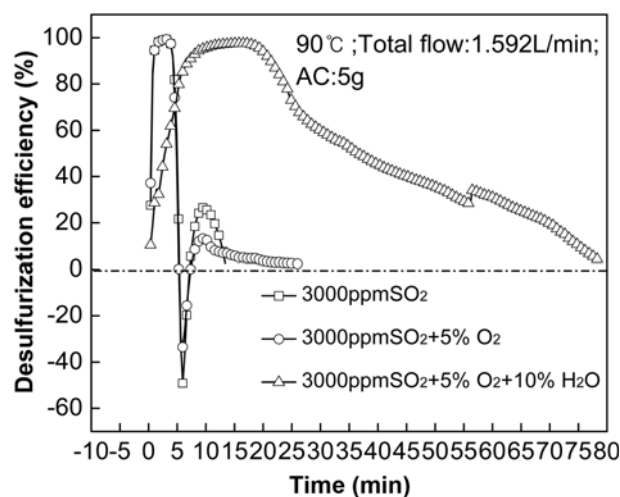

Fig. 4. AC desulfurization efficiency varies with time in SO_2, SO_2+O_2 and $SO_2+O_2+H_2O$ atmosphere respectively at 90 °C.

crease rapidly. This indicates that O_2 is necessary for SO_2 adsorption and conversion process. On the basis of previous research results, it is considered that SO_3 which comes from the reaction of O_2 and SO_2 can react with H_2O (g) to form H_2SO_4 (g). The consumption of SO_3 promotes the SO_2 oxidation and makes SO_2 adsorption sites vacant. It creates the conditions for further SO_2 adsorption.

1-2. Effect of H_2O on SO_2 Conversion Process

H_2O plays a key role in AC desulfurization process. To obtain the effect mechanism of H_2O in AC desulfurization process, AC adsorption capacity in SO_2, SO_2+O_2 and $SO_2+O_2+H_2O$ atmospheres at the same temperature are compared. The results are shown in Fig. 4. According to the result of Fig. 4, the presence of H_2O greatly extends the adsorption saturation time of AC. Saturation sulfur retention under three kinds of adsorption conditions at 90 °C was calculated. AC saturation sulfur retention (52.6 mg/g) in $SO_2+O_2+H_2O$ atmosphere is 4.6 times as much as that (11.4 mg/g) in SO_2+O_2 atmosphere and 5.0 times as much as that (10.6 mg/g) in SO_2+O_2 atmosphere. It has been shown that [20] when the concentration of SO_3 in flue gas arrives to 1 ppm, the H_2SO_4 dew point is 113 °C. The concentration of SO_3 in AC interior is much higher than 1 ppm in our research. Therefore, the actual dew point temperature will be higher than 113 °C. Sulfuric acid vapor in AC interior condenses rapidly and exists in the form of liquid sulfuric acid in AC pores. For this reason, it is considered that condensation breaks the equilibrium and promotes the reaction of SO_3 and H_2O (g), and ultimately reflects the SO_2 adsorption capacity upgrading. The ion chromatograph analysis in our test shows that there is only SO_4^{2-} in the AC immersing solution in $SO_2+O_2+H_2O$ atmosphere. This indicates that all adsorbed SO_2 in AC interior forms sulfuric acid due to the effect of water.

1-3. Effects of O_2 and H_2O Concentration on AC Desulfurization Activity

Effects of O_2 and H_2O concentration in $SO_2+O_2+H_2O$ atmosphere are studied to further get a clearer understanding of O_2 and H_2O effect mechanism. SO_2 adsorption curves at the temperature of 60 °C are shown in Fig. 5(a) and (b). AC desulfurization efficiency increases with the increase of O_2 concentration, and when O_2 concentration

Fig. 3. Influence of O_2 in $SO_2+O_2+H_2O$ atmosphere: O_2 was added or removed at 10 minutes, 30 minutes and 50 minutes to study the necessity of O_2 at 60 °C.
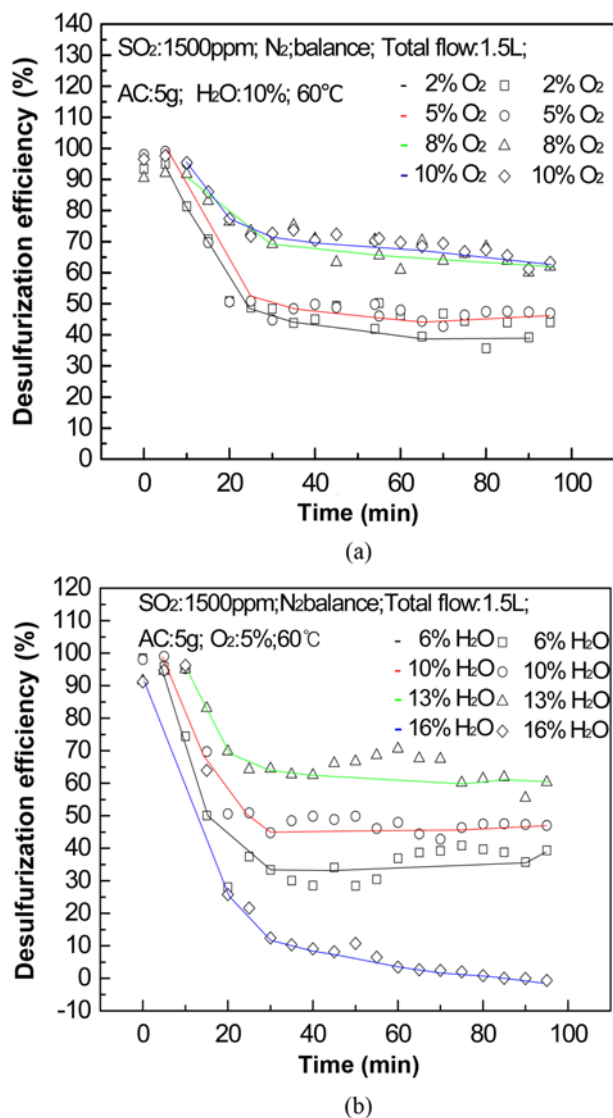
(a)

(b)

Fig. 5. Effects of O₂ and H₂O concentrations on SO₂ conversion efficiency: the curves of figure (a) was effect of O₂ concentration (2%, 5%, 8%, 10%) on desulfurization efficiency under the condition of 60 °C and 10% H₂O; the curves of figure (b) was effect of H₂O concentration (6%, 10%, 13%, 16%) on desulfurization efficiency under the condition of 60 °C and 5% O₂; Lines with different color represent the trends of date points.
(a) Effects of O₂ concentrations on SO₂ removal efficiency,
(b) Effects of H₂O concentration on SO₂ removal efficiency

exceeds 8%, desulfurization efficiency is essentially the same. AC desulfurization reaction is a heterogeneous catalytic reaction. Only when oxygen in flue gas diffuses to the catalytic oxidation active site in surface of AC can it react with chemical adsorbed SO_2 in active site to form SO_3. When O_2 concentration is relatively low, O_2 diffusion resistance is very large. Although the apparent molar ratio of O_2 and SO_2 is greater than 0.5, O_2 molecules which diffuse to the catalytic oxidation active site are rare and oxidized SO_2 is also little. Increase of O_2 concentration can reduce the diffusion resistance and increase the probability of oxygen diffusion to the active site, which increases the chance of SO_2 being oxidized to SO_3 and

further promotes the combination of SO_3 and H_2O (g), and ultimately reflects the SO_2 adsorption capacity upgrading. When O_2 concentration is much greater than the SO_2 concentration, O_2 can almost diffuse to all catalytic oxidation active sites in the surface of AC and the increase of O_2 concentration has no effect on AC desulfurization activity. When H_2O concentration varies from 6% to 13%, AC desulfurization efficiency significantly improves with increasing H_2O volume fraction. This is because the higher the H_2O concentration is, the more water molecules diffuse to the AC interior. Hence, this increases the probability of the combination of SO_3 and H_2O, and ultimately reflects desulfurization capacity upgrading. When H_2O concentration changes from 13% to 16%, AC desulfurization efficiency decreases significantly. This can be proved by the analysis of AC pore structures and H_2O steam properties. According to previous research [7.9], micropores of AC is SO_2 adsorption and conversion place. Molecular collision diameters of SO_2, O_2 and H_2O are 0.4112nm, 0.3467 nm and 0.2641 nm, respectively. These molecules can diffuse to the micropores of 2 nm. Different from O_2 and SO_2, H_2O (g) can condense into liquid H_2O rapidly in micropores and form water film [12]. When H_2O concentration is too high, H_2O (g) will form excess water film, which can plug the pores and flood active sites and ultimately hinder the diffusion of SO_2 and O_2 to micropores.

1-4. SO₂ Conversion Mechanism and Sulfur Enrichment Form

From the above research, the existence of SO_3 and H_2SO_4 in AC interior is proved in the presence of O_2 and H_2O, and effect of O_2 and H_2O concentration on AC desulfurization activity is analyzed. According to our research and combining with previous research of most scholars [4-17], detailed reactions of AC desulfurization process are proposed as follows:

(a) $SO_2(g) \rightarrow SO_2$(physically adsorbed);
(b) $SO_2(g)$+Active Site$\rightarrow SO_2$(chemical adsorbed);
(c) SO_2(chemical adsorbed)+$O_2 \rightarrow SO_3$+Active Site;
(d) SO_2(physically adsorbed)+Active SiteSO_2(chemical adsorbed);
(e) SO_3+$H_2O(g) \rightarrow H_2SO_4(g)$;
(f) $H_2SO_4(g) \rightarrow H_2SO_4(l)$.

From the above mechanism, Steps (c) and (e) are key steps in the process. The presence of O_2 and H_2O is a necessary condition for AC desulfurization behavior. Step (a), SO_2 physical adsorption is just a transitional step of SO_2 conversion. Step (f), condensation of sulfuric acid vapor is assumed the rate controlling step of the whole process. The series of reactions take place in AC micropores. The final reaction product, liquid sulfuric acid, may also overflow from the micropores and enrich in the mesopores or macropores.

2. Sulfuric Acid Desorption Mechanism by Composite Regeneration

We proposed a new regeneration method which combines the advantages of both heating regeneration and water scrubbing regeneration, adding water vapor blowing in heating regeneration process, called combined regeneration. Sulfuric acid desorption mechanism by this method was studied.

2-1. Effect of Water Vapor Blowing on Regenerative ACs Microstructure

AC quality loss is unavoidable in regeneration process. Firstly, AC quality losses of different regeneration methods (heating regeneration, water scrubbing regeneration, combined regeneration) are compared in Fig. 6. AC quality loss of heating regeneration is much
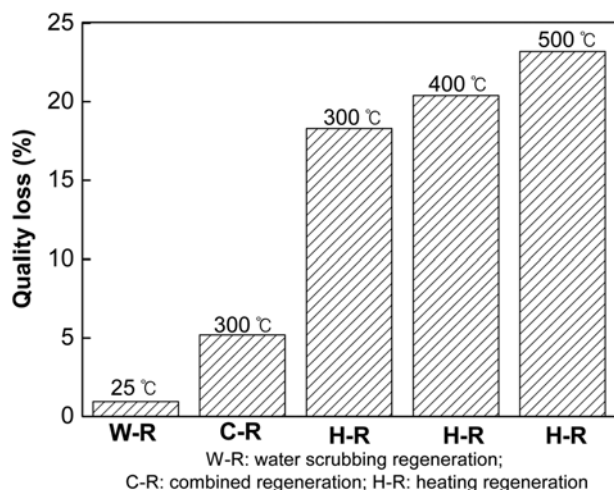
Fig. 6. Quality loss of regeneration one time AC by heating regeneration (temperature of 300 °C, 400 °C and 500 °C), water scrubbing regeneration (temperature of 400 °C) and combined regeneration (temperature of 300 °C).

C-R: combined regeneration; H-R: heating regeneration

Fig. 7. Adsorption isotherms of ACs: N$_2$ adsorption isotherms (relative pressure 0.001-1) of ACs by heating regeneration and combined regeneration were compared to study the changes of AC pore structures.

higher than that of water scrubbing regeneration and combined regeneration. With the heating regeneration temperature increase, AC quality loss apparently increases. At the same heating temperature (300 °C), quality loss (5.2%) in combined regeneration is obviously lower than that (18.3%) in heating regeneration. In addition, we can see that AC quality loss in water scrubbing regeneration is the lowest, only 0.95%. In heating regeneration process, adsorbate H$_2$SO$_4$ forming in SO$_2$ removal process reacts with carbon of AC interior and resolves in the form of SO$_2$ (C+2H$_2$SO$_4$=CO$_2$+2SO$_2$+2H$_2$O; C+H$_2$SO$_4$=CO+SO$_2$+H$_2$O [17.19]). The reactions release the space of AC pores and recover AC repeated desulfurization property. Meanwhile, the chemical loss of carbon is not negligible. That is why quality loss in heating regeneration is the highest. In water scrubbing regeneration process, large amounts of water are used to wash adsorbate H$_2$SO$_4$, and low concentration sulfuric acid is collected [17]. In contrast to heating regeneration, the principle of water scrubbing regeneration is simple, just relying on concentration difference and no chemical loss of carbon comes up. That is why quality loss of water scrubbing regeneration is the lowest. Quality loss of combined regeneration is lower than that of heating regeneration. It explains that water vapor blowing reduces the chemical loss of carbon. To further understand the effect of water vapor blowing, desulfurization-regeneration repeated experiments are carried out. Re-
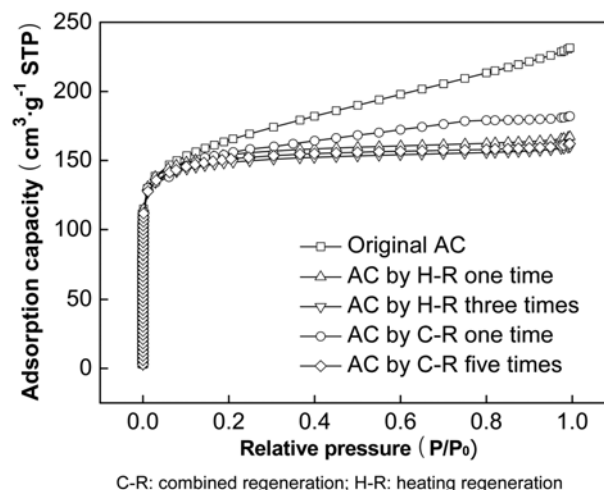
generation temperature keeps at 400 °C. The results show that AC cumulative quality loss (53.6%) of five-times in combined regeneration is still less than that (62.4%) of three-times in heating regeneration.

N$_2$ adsorption isotherms (relative pressure 0.001-1) and pore structure parameters are obtained to study the effect of water vapor blowing on AC pore structures. The results are shown in Fig. 7 and Table 3. From Fig. 7 we can see that adsorption isotherm of original AC shows obvious smearing effect, which indicates that there are some mesopores in AC. So it presents mesopore-filled characteristics, and it also can be concluded from Table 3 by comparing pore volumes of micropore and mesopore. Adsorption isotherms of ACs after regeneration are typical I type adsorption isotherms with micropore-filled characteristic. By analyzing effects of water vapor blowing on adsorption isotherm of AC after regeneration, it is found that adsorption isotherms of AC through one-time regeneration have great difference compared to that of original AC. From the pore structure parameters in Table 3, micropore areas and micropore volumes after heating regeneration are bigger than that of original AC, but it has less BET surface area, total pore volume and mesopore volume. It can be concluded that micropores are produced and enriched while mesopores are destroyed. AC is a kind of activated carbon material which is not completely activated and part of micropores

Table 3. Pore structure parameters of ACs

Samples	BET surface area (m$^2 \cdot$g^{-1})	Total pore volume (cm$^3 \cdot$g^{-1})	Micropore surface area (m$^2 \cdot$g^{-1})	Micropore volume (cm$^3 \cdot$g^{-1})	Mesopore volume (cm$^3 \cdot$g^{-1})
Original AC	563.144	0.354	308.191	0.143	0.182
AC by H-R[a] 1 time	531.265	0.285	376.138	0.174	0.051
AC by H-R 3 times	509.616	0.249	403.551	0.187	0.031
AC by C-R[b] 1 time	544.679	0.325	336.289	0.159	0.106
AC by C-R 5 times	519.710	0.256	414.369	0.192	0.035

[a]H-R: heating regeneration
[b]C-R: combined regeneration

in AC interior are plugged by tar and amorphous carbon. Heating regeneration plays a role of reactivation, and it has the effect of pore-making and pore-reaming. On one hand, tar and amorphous carbon are burn-lossed, and the plugging micropores are opened; for the other, mesopores are expanded. However, mesopores would disappear if the mesopores were expanded too much. As seen from Fig. 7, compared to AC only through heating regeneration, the adsorption isotherm of AC after combined regeneration one time is more close to that of the original AC. As shown in Table 3, increasing extent of micropore areas and micropore volumes by combined regeneration is less than that of heating regeneration, so is it with decreasing extent of BET specific surface areas, total pore volumes and mesopore volumes. The reason is that water vapor blowing has the effect of activity protection and preventing reactivation. Pore structure of AC changes less during combined regeneration than that during heating regeneration.

The surface functional groups of original AC, AC by heating regeneration and composite regeneration are confirmed by FT-IR (Fig. 8). From Fig. 8(a), bands at $1,150\,cm^{-1}$, $1,550\,cm^{-1}$, $3,500\,cm^{-1}$ are

Table 4. Contents of SO_3^{2-} and SO_4^{2-} in NaOH solution absorbing desorption products

ACs	Contents of SO_3^{2-} (mmol)	Contents of SO_4^{2-} (mmol)
H-R: 300	0.0421	0.0091
H-R: 400	0.0465	0.0076
H-R: 500	0.0478	0.0056
C-R: 300	0.0157	0.0334
W-R[a]: 25	0.0021	0.0264

[a]W-R: water scrubbing regeneration

C-O, C=O, O-H, respectively [21]. It is necessary to underline that band $2,400\,cm^{-1}$ is physically CO_2 from air. By analyzing the results of AC characterization after heating regeneration one time and three times, it is found that types of AC surface functional groups by heating regeneration one time are basically the same with the original AC, However, FTIR spectrum of AC by heating regeneration three times has obvious changes in contrast to original AC, the O-H functional groups tend to disappear. As Fig. 8(b) shows, FTIR spectrum of AC by combined regeneration five times is basically the same with original AC. This indicates that the surface functional groups of AC virtually make no change by combined regeneration which added water vapor blowing in heating regeneration process.

2-2. Effect Mechanism of Water Vapor Blowing on Sulfuric Acid Desorption

Water vapor blowing in heating regeneration process inhibits reactivation effect, and as a result reduces the change of AC pore structure and surface functional groups. To further understand the effect mechanism of water vapor on sulfuric acid desorption, the content of SO_3^{2-} and SO_4^{2-} in NaOH solution which absorbs desorption products is detected with ion chromatograph in our test. The results are shown in Table 4. In desorption products of heating regeneration, the content of SO_3^{2-} is much higher than that of SO_4^{2-}. This shows that large amounts of SO_2 exist in desorption gas. The production of sulfur dioxide is the result of redox reactions between H_2SO_4 and carbon (described above). In desorption products of water scrubbing regeneration, the content of SO_4^{2-} is almost ten times higher than that of SO_3^{2-}. However, the total amount of sulfur desorption is apparently less than that of heating regeneration because of incomplete regeneration in water scrubbing regeneration. The content ratio of SO_3^{2-} to SO_4^{2-} in combined regeneration products is opposite to heating regeneration. The content of SO_4^{2-} is obviously higher than that of SO_3^{2-}. This explains that sulfur enriched in desulfurization process desorbs mostly in the form of +6 valence. Following the SO_2 removal mechanism in presence of O_2 and H_2O (described in section 1), SO_2 reacts with active sites, O_2, and H_2O, ultimately produces liquid sulfuric acid stored in AC pores. On the basis of this conclusion, we consider that part of the liquid sulfuric acid arrives at boiling point due to the high temperature (more than $300\,°C$) in regeneration, and consequently turns into sulfuric acid vapor, and is carried out by water vapor blowing. The amounts of sulfuric acid vapor depend on the ratio of reaction between H_2SO_4 and carbon to volatilization of liquid sulfuric acid. Combined with the SO_2 removal process, the rules of sulfur pattern transition in AC interior in the whole desulfurization and regeneration process can be concluded, as Fig. 9 shows.

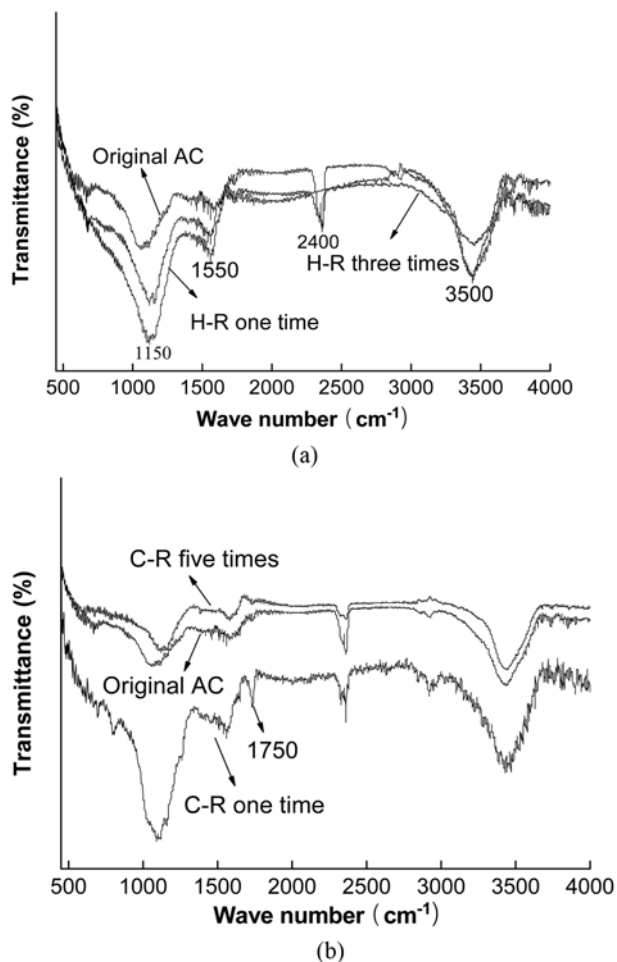C-R: combined regeneration; H-R: heating regeneration

Fig. 8. FTIR spectra of ACs: The surface functional groups of original AC, AC by heating regeneration and combined regeneration are confirmed by FT-IR.
(a) FTIR spectra of original AC and heating regeneration AC,
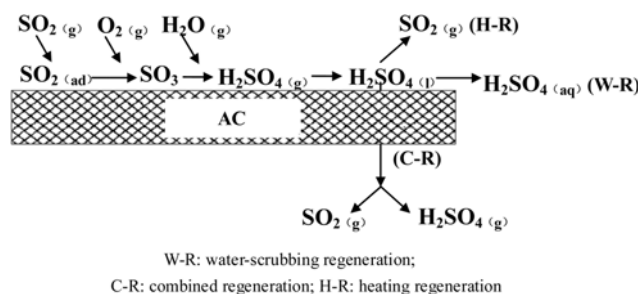(b) FTIR spectra of original AC and combined regeneration AC

Fig. 9. Sulfur conversion schematic in AC desulfurization-regeneration process by heating regeneration, water scrubbing regeneration and combined regeneration.

As observed in Fig. 9, in combined regeneration process, the proportion of adsorbate H_2SO_4 which reacts with carbon decreases due to the influence of water vapor blowing. It reduces the cost of carbon, which builds up the pore structure of AC and inhibits reactivation effect, and as a result reduces the change of AC pore structure and surface functional groups.

CONCLUSION

Commercial activated coke was used to study the mechanism of SO_2 removal in the presence of O_2 and H_2O and desorption mechanism of adsorbate H_2SO_4. With the participation of O_2 and H_2O, SO_2 can be oxidized to SO_3 and converted into H_2SO_4 which exists in the form of liquid. Condensation of sulfuric acid vapor is assumed the rate controlling step of the whole process. Compared with heating regeneration, water vapor blowing in combined regeneration inhibits the reaction between H_2SO_4 and carbon, and consequently reduces the chemical loss of carbon, which makes AC pore structure and surface functional groups change little. Adsorbate H_2SO_4 evaporates to sulfuric acid vapor due to the high temperature in regeneration, and is carried out by water vapor blowing. In addition, the amount of sulfur desorption in combined regeneration is much more than water scrubbing, AC regenerates thoroughly. Combined regeneration is a promising regeneration method for desulfurization AC and needs further research.

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