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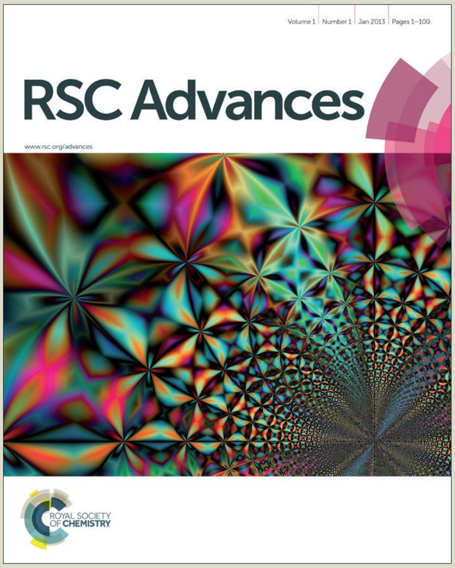

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Studies on Flue Gas Desulfurization Using EDA/SiO_2-Phosphoric Acid Solution as an Absorbent

Wen Bo [1], Junjie Zhang [2], Hongxia Li [1] and Xiangjia Song [1]

Flue gas desulfurization by immobilized amine is a new desulfurization technique. The EDA/SiO_2 and the additive H_3PO_4 were used as desulphur absorber. SO_2 was absorbed by the system and desorbed from the loaded solution. And the cycle operation was also analyzed in the experiments. Some technology conditions such as the amount of EDA/SiO_2, the temperature, concentration of SO_2 and pH value were experimentally researched. With the optimized process, the absorption efficiency of this system could reach 98% and the desorption efficiency was over 50%, showing good absorption/desorption capability and promising potential to be applied in desulphur area.

1 Introduction

It is well known that exhaust gas of coal is the main reason of air pollution in the world. In China's energy consumption structure, coal accounts for 76.12% [1]. Many pollutants are emitted during coal utilization, among which SO_2 is one of the biggest harmful emissions. SO_2 is not only leads to the acid rain, but also has the serious harm to the respiratory system of human being. Various desulfurization technologies have been developed to reduce pollutant emission.

Based on the morphology of desulfurization products, the methods of flue gas desulfurization can be divided into three types: dry, wet and semi-dry. Dry process mainly includes oxidative desulfurization (ODS), oxidation–extraction desulfurization (OEDS), pulse plasma chemical process (PPCP) and adsorptive desulfurization (physical adsorption desulfurization, activated adsorption desulfurization) [2]. Wet process mainly includes limestone-gypsum method [3, 4], seawater method, citric acid-sodium citrate buffer solutions method [5], sodium salt cycling method, magnesia method and alkali aluminum sulfate-gypsum method. And semi-dry desulfurization mainly includes spray-drying process [6]. However, one big issue of those techniques is that desulphur waste will re-pollute environment. Therefore, it is necessary to develop a novel desulfurization technique with both good environmental and economical properity

Ethylenediamine (EDA) has been intensively investigated recently as a wet desulfurization due to its high desulfurization efficiency for desulfurization[7], low corrosivity and no re-pollution. 2-1: However, some concerns about EDA must be overcome, such as poor oxidation stability, low bubble temperature and releasing amine during flue gas desulfurization (FGD) process [8]. It is necessary to find better desulfurizer to solve these problems.

In this paper, an EDA immobilized on SiO_2 material (EDA/SiO_2) was synthesized. As a desulphur absorber, it shows very promising properties and can achieve a good SO_2 absorption efficiency. 2-1: This material has many advantages, such as low cost, high desulfurization efficiency, recycling absorbent, low amine loss and no re-pollution.

2 Desulfurization Mechanism of EDA/SiO_2

SO_2 has a remarkable solubility in water, while on the other hand it can also dissociate with water. The equations of ionization in water are showed below:

$$SO_2(g) \leftrightharpoons SO_2(aq) \qquad (1)$$

$$SO_2(aq)+H_2 \leftrightharpoons OH^{+}+HSO_3^{-} \qquad (2)$$

$$HSO_3^{-} \leftrightharpoons H^{+}+SO_3^{2-} \qquad (3)$$

With the increasing of the H_2SO_3 concentration in solution, reaction (1) (2) move to right and the $[H^+]$ increase. The reactions finally can reach equilibrium and no more SO_2 can be dissolved in the solution. In order to increase the solubility of SO_2, the $[H^+]$ should be decreased, which can be realized by adding phosphoric acid in the solution.

The structure of EDA/SiO_2 is showed in Fig.1.

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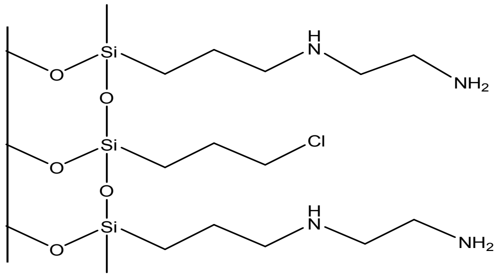


Fig.1 The structure of EDA/SiO_2

EDA has plurality of amine groups and it is a kind polyamine. The process of adsorption and desorption are shown as follows.

$$NH_2CH_2CH_2NH_2 + HX \xrightarrow{protonation} NH_2CH_2CH_2NH_3^{+} + X^{-} \quad (4)$$

$$NH_2CH_2CH_2NH_3^{+} + SO_2 + H_2O \xrightarrow{absorption} NH_2CH_2CH_2NH_3^{+} + HSO_3^{-} \quad (5)$$

$$NH_2CH_2CH_2NH_3^{+} + HSO_3^{-} \xrightarrow{desorption} NH_2CH_2CH_2NH_3^{+} + SO_2 + H_2O \quad (6)$$

1-2: In the reaction (4), EDA has two amine groups, one of which can combine with H^{+} and generate protonated amine. Protonated amine is relatively stable, and can be better desorbed after the absorption of SO_2. The characteristics of anion X^{-} can influence the desulfurization process. If the anion is Cl^{-}, the causticity of the absorbent is increased. Also, SO_4^{2-} is not suitable because it influences the recovery of the absorbent. Part of SO_2 is oxidized into SO_4^{2-} in the FGD process, which should be removed in order to keep the absorption capacity of the absorbent. Also, considering the excellent buffer effect and anti-oxidation of PO_4^{3-} in the sodium phosphate method, phosphoric acid is chosen as the best additive. Reaction (5) is a process of SO_2 absorbed by amine. Reaction (6) is a process about the regeneration of EDA/SiO_2.

3 Experimental Section

3.1 Materials

The simulated flue gas was prepared by air comes from air compressor and SO_2 comes from a SO_2 generator, respectively. SO_2 was synthesized by decomposition of Na_2SO_3 with H_2SO_4. 1-9: In each condition of the experiment, there is an equal amount of CO_2 in the flue gas. Since the solubility of SO_2 is greater than that of CO_2, the influence of CO_2 in the flue gas was not considered.

1-3(1-8, 2-2): The absorption solution was prepared by EDA, SiO_2, γ-Chloropropyltrichlorosiane (CPTCS) and 40mL deionized water. Phosphoric acid was used to adjust the pH value of the solution

EDA was purchased from Shanghai Jingchun Chemical Regent Co. Phosphoric acid (purity⩾85%; the other component is water) was purchased from Tianjin Tianda Chemical Regent Plant. SiO_2 was purchased from Tianjin Baishi Chemical Regent Co. CPTCS was purchased from Zibo Qiquan Chemical Regent Co.

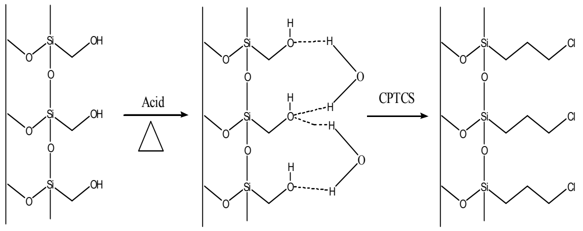
3.2 The Preparation of EDA/SiO_2

Activation of SiO_2: 30g of SiO_2 was added into 1mol/L of nitric acid solution and refluxed at 383K with stirring for 16 h. Then the product was washed to neutral with deionized water and carbinol, and dried in vacuum at the temperature of 383K. The dried material was activated SiO_2.

Hydration of SiO_2 was performed by putting the activated SiO_2 into constant temperature hydration device for 16h at a constant temperature of 298K.

Alkylation reaction: 50mL of dehydrated n-hexane and 30mL of CPTCS were mixed with the activated SiO_2, and the mixture was refluxed gently 16 hours in water bath at the temperature of 298K. Product was washed to neutral by n-hexane, carbinol and deionized water, respectively. Then the product was dried in vacuum at a temperature of 363K and CPTCS-SiO_2 was got.

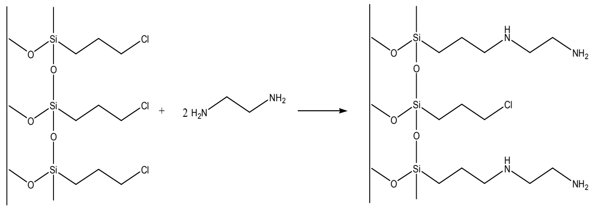
The synthesis route of CPTCS-SiO_2 is showed as follow:



(7)

Preparation of EDA/SiO_2: 1-4: 20g of CPTCS-SiO_2 was dispersed into a mixture of 30mL of carbinol and 40mL of EDA, and the suspension was stirred for 16 hours at a temperature of 333K. The product was washed to neutral by carbinol, deionized water and ammonia, respectively. Then it was dried in vacuum at a temperature of 363K and EDA/SiO_2 was got.

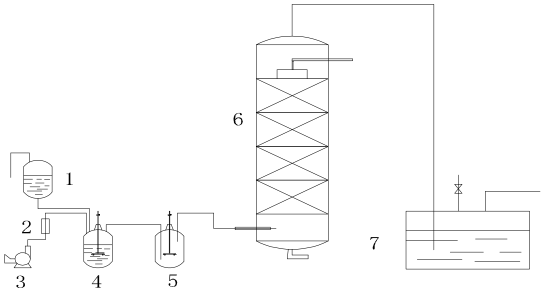
The synthesis route of EDA/SiO_2 is as follows:



(8)

3.3 Experimental Apparatus and Methods

Figure 2 shows a schematic map of flue gas desulfurization process by the EDA/SiO_2 - phosphoric acid system. Na_2SO_3 bottle and H_2SO_4 bottle were used to prepare SO_2. Air from an air pump and SO_2 flowed through the flowmeter, mixed at the manostat bottle and then flowed through the absorption tower. NaOH was used in tail gas treatment tank to react with the SO_2 which was not absorbed in absorption tower.



(1) Na_2SO_3 bottle; (2) flowmeter; (3) air pump; (4) H_2SO_4 bottle; (5) manostat bottle; (6) absorption tower; (7) tail gas treatment tank.

Fig.2 Technological process of absorption about desulfurization

3.4 Count Method of Absorption and Desorption Efficiency

AE is defined as the desulfurization percentage to evaluate the absorption effects:

$$\mathrm{AE} = \frac{y_i - y_o}{y_i} \times 100\% \tag{9}$$

where y_i is the inlet concentration of SO_2 in the gas phase and y_o is the outlet gas concentration of SO_2 after absorption.

DE is defined as the desorption percentage to evaluate the desorption effects:

$$\mathrm{DE} = \frac{x_i - x_o}{x_i - x_\varphi} \times 100\% \tag{10}$$

where x_i denotes the inlet concentration of SO_2 in loaded absorption solutions and x_o denotes the outlet concentration of SO_2 in unloaded solutions after desorption. When absorption is used repeatedly, x_φ represents the initial SO_2 concentration before absorption. If a fresh absorption solution is prepared and used for first time, x_φ is equal to zero.

3.5 Analytical Methods

The concentration of SO_2 in the flue gas and in the aqueous solution was analyzed by the iodine method, as was recommended in the literature.[9, 10]

4 Results and Discussion

4.1 Physical property of EDA/SiO_2

2-1: EDA/SiO_2 is a kind of milky particle which is semitransparent and spherical. Its particle size is 150-250μm, aperture is 40-70A°, pore volume is 0.60-0.85ml/g and specific surface area is 400-600m^2/g. The surface morphology of EDA/SiO_2 is shown in Figure 3. It can be seen that the overall structure of the material is loose, which is favorable for the adsorption and desorption.

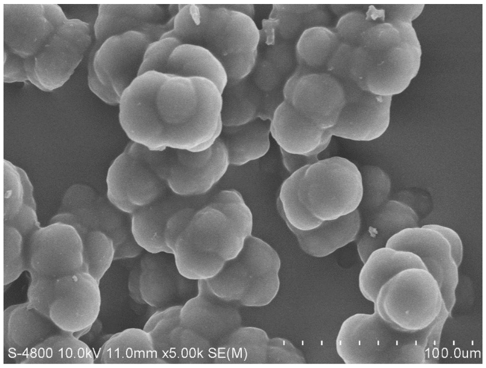


Fig.3 The SEM image of EDA/SiO_2

4.2 Effect of the EDA/SiO_2 Amount in an Absorption Solution

Figure 4 shows the effects of EDA/SiO_2 amount in the absorption solution on absorption efficiency. 2-2: 0.2g, 0.4g, 0.6g, 0.8g and 1.0g of EDA/SiO_2 were put into 40mL of water and phosphoric acid was used to control the pH of the solution. It can be seen slope curve was observed as the EDA/SiO_2 less than 0.4g and then a maxium like value was reached as the mount of EAD/SiO_2 over 0.4g. This phenomenon was related to the concentration of effective amine groups in the solution.

At small EDA/SiO_2 amount, the effective amine groups increase. Therefore the absorption efficiency increased. But if the amount of EDA/SiO_2 was too big, it will lead to the combination of SO_2 with EDA/SiO_2 and it is difficult to desorb for absorbed SO_2, which is not good at the cyclic utilization of absorption material. 1-6: So, the suitable amount of EDA/SiO_2 is set as 0.4g in 40mL water.

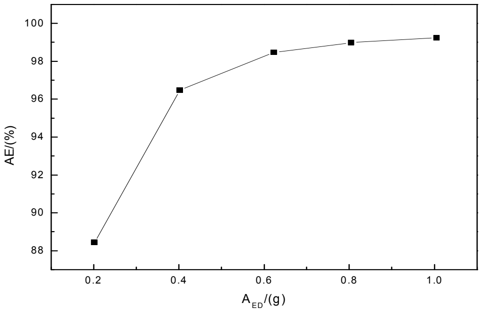


Fig.4 Effects of the EDA/SiO_2 amount on absorption
(experimental conditions: flow rate of gas *G*= 400ml/min; preheat temperature *t*=60 °C; pH=6.0~6.5; the concentration of SO_2 C=3000mg/m^3; adsorption time is 60 minutes)

The amount of EDA/SiO_2 in solution also affects the desorption efficiency, as shown in Figure 5. With the amount of EDA/SiO_2 increase, the desorption efficiency decreased, which was associated with the inhibition of alkali (the alkali was from the reaction of EDA/SiO_2 with water). The more alkalinity of the loaded solution, the less ideal of the desorption efficiency.

With the amount of EDA/SiO_2 increase, desorption becomes difficult. The reason for that phenomenon is that EDA has two NH_2 groups and one of them is more active to react with SO_2 to form the corresponding salt, which is difficult to decompose at desorption process by heating.[11].

Since SO_2 is acidic gas, higher amount of EDA/SiO_2 with strong basicity is favorite for absorption but is harmful for desorption. Based on previous results, 1-6: the optimized amount of EDA/SiO_2 was fixed at 0.4g in 40mL water. In this condition, the corresponding absorption desorption efficiency were more than 98% and 50%, respectively.

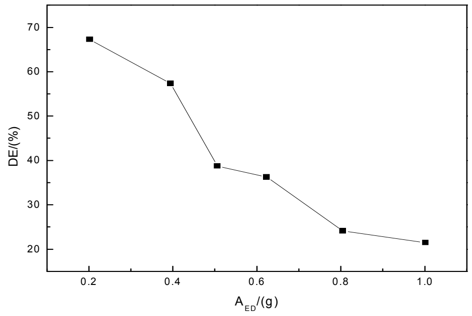


Fig.5 Effects of the EDA/SiO_2 amount on desorption

(experimental conditions: initial concentration of SO_2 in the loaded solution *w*=1.8g/L; preheating temperature *t* =70 °C; initial pH of the loaded solution pH=5; desorption time is 60min)

4.3 Effect of Temperature

Figure 6 shows the effects of temperature on absorption efficiency, where the desulfurization efficiency decreased with the increase of temperature. When the temperature was over 60℃, absorption efficiency decreased quickly.

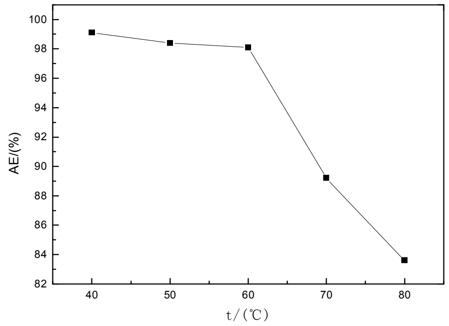


Fig.6 Effects of the temperature on absorption

(experimental conditions: flow rate of gas *G*= 400ml/min; amount of EDA/SiO_2 *A*= 0.4g in 40mL water; pH=6.0~6.5; the concentration of SO_2 C=3000mg/m^3; adsorption time is 60 minutes)

On the one hand, the temperature affects mass transfer. The equation of convective mass transfer rate can be defined from the following relation:

$$N_A=k_G\,(p_A-p_{Ai}) \qquad (11)$$

where N_A denotes the convective mass transfer rate of solute A, k_G denotes the gas film mass transfer coefficient, p_A denotes the partial pressure of solute A in gas phase and p_{Ai} denotes the partial pressure of solute A at the interface.

It is well known that when other parameters are stable, the value of gas film mass transfer coefficient k_G increases as temperature decreasing. Therefore, low temperature favorites the absorption of SO_2.

In addition, since the SO_2 absorption is an exothermal reaction, low temperature is also helpful for the desulfurization process. However controlling low temperature consumes much more energy. In order to balance the cost and absorption efficiency, the optimum temperature was set at 60 °C.

Figure 7 shows the effects of the preheat temperature on desorption efficiency. It can be seen that the desorption efficiency increased as the temperature rising. However, when the temperature was over 70 °C, the desorption efficiency became stable and the system reached its maximum capability.

Desorption is an inverse process of absorption because the mass transfer direction of desorption is directly opposite to absorption. Temperature increasing is not conducive to absorption, but is conducive to desorption. But in actual industrial operation, much higher temperature may cause higher energy consumption for heating, so 70 °C is considered to be the suitable temperature.

4.4 Effect of SO_2 Concentration

The effect of the concentration of SO_2 on absorption efficiency is shown in Figure 8. The data indicate that the desulfurization efficiency increases with the decreasing of the SO_2 concentration in flue gas.

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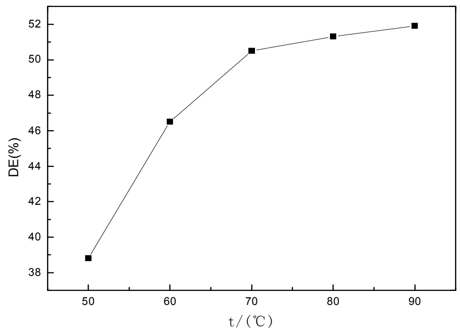

Fig.7 Effects of temperature on desorption
(experimental conditions: initial concentration of SO_2 in the loaded solution *w*=1.8g/L; amount of EDA/SiO_2 *A*=0.4g in 40mL water; initial pH of the loaded solution pH=5; desorption time is 60min)

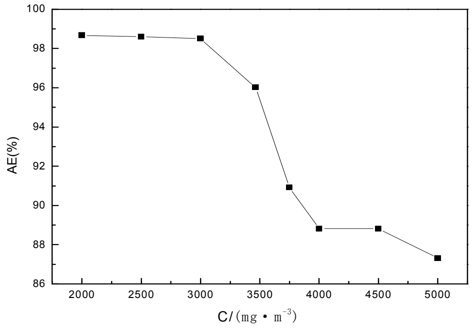

Fig.8 Effects of the initial SO_2 concentration on absorption
(experimental conditions: flow rate of gas *G*= 400ml/min; amount of EDA/SiO_2 *A*=0.4g in 40mL water; pH=6.0~6.5; preheat temperature *t*=60 °C; adsorption time is 60 minutes).

The concentration of SO_2 in flue gas increase will promote the ability of SO_2 diffusion to the internal liquid through the solution surface and then accelerate the speed of reaction. But the higher SO_2 concentration will lead to part of SO_2 cannot be absorbed by the absorber. Therefore, higher concentration of SO_2 will make absorption efficiency decrease.

Figure 9 shows the effects of the SO_2 concentration in solution on desorption. From the aspect of chemical equilibrium, the increase of the SO_2 concentration will lead the movement of chemical equilibrium to the direction of desorption. But if the SO_2 concentration is too big, it will influence the recycling of absorbent. So in this investigation, the initial SO_2 concentration is specified as 1.8g/L.

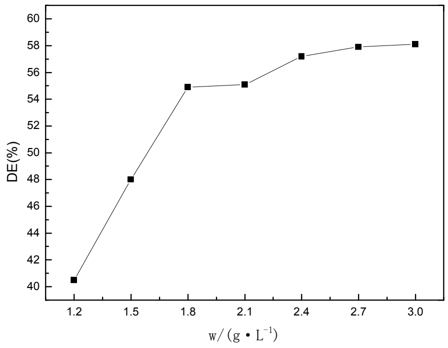

Fig.9 Effects of the SO_2 concentration on desorption
(experimental conditions: amount of EDA/SiO_2 *A*=0.4g in 40mL water; initial pH of the loaded solution pH=5; preheating temperature *t* =70 °C; desorption time is 60min)

4.5 Effect of pH

Figure 10 shows the effects of pH on absorption. The pH value of the absorption agent is adjusted by tuning the ratio of H_3PO_4 and EDA/SiO_2 in the system. The results indicated that the desulfurization efficiency for AE increases with pH value increase.

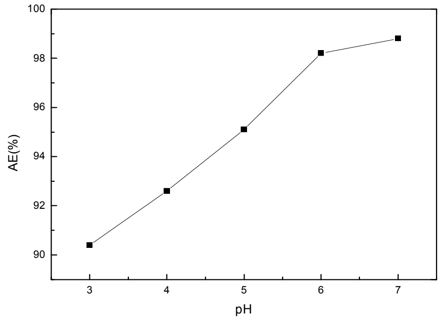

Fig.10 Effects of the pH on absorption
(experimental conditions: flow rate of gas *G*= 400ml/min; amount of EDA/SiO_2 *A*=0.4g in 40mL water; preheat temperature *t*=60 °C; concentration of SO_2 C=3000mg/m^3; adsorption time is 60 minutes).

With the increase of the pH value, the free active amines in solution increase, and the buffer capacity increase. So it will easy for absorption liquid to combine with SO_2 and desulfurization efficiency increases. From the aspect of chemical equilibrium, the increase of pH value inhibits the [H^+], and chemical equilibrium moves to right direction, so desulfurization efficiency increases. However, at high pH, the selectivity of EDA/SiO_2 between CO_2 and SO_2 would decrease. Therefore, the pH range was optimized from 6.0 to 6.5.

Figure 11 shows the pH effect on desorption. The results indicate that desorption efficiency decreases with the pH value increase. The stronger of the loaded solution acid is, the higher of desorption efficiency is. While the initial pH value of the loaded solution is largely determined by the absorption amount of SO_2 and the initial pH value of absorption solution.

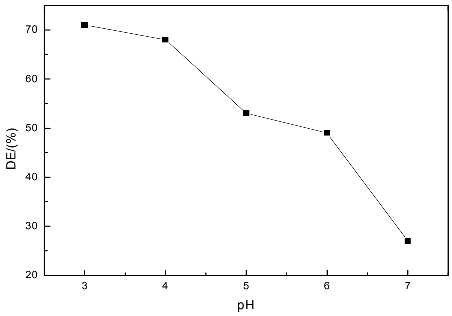

Fig.11 Effects of the pH on desorption
(experimental conditions: initial concentration of SO_2 in the loaded solution *w*=1.8g/L; amount of EDA/SiO_2 *A*=0.4g in 40mL water; preheating temperature *t* =70 °C; desorption time is 60min)

This is because a decrease of [H^+] with an increase of the pH value strengthens the combined ability of the absorption agent with SO_2. But after absorb SO_2; pH value of loaded solution becomes lower. Strong acid of loaded solution will not only have influence on the effect of absorption, but also increase corrosion to equipment. So the suitable pH value is specified as 5.0.

4.6 Circulating experiment

In order to investigate the desulfurization capability of the absorption reagent after regeneration, the absorption-desorption cycles were performed several times. The experimental results are shown in Figure 12 and Figure 13.

As shown in Figure 12, the absorption efficiency of SO_2 in EDA/SiO_2 - phosphoric acid system decreased as the number of cycles increased. After nine cycles, absorption efficiency is maintained at about 91%. The fading of the absorption efficiency of the solution at the initial stage (less than 9 cycles) was related to the oxidation of SO_2 to SO_3 and SO_3 was difficult to be released from the solution.

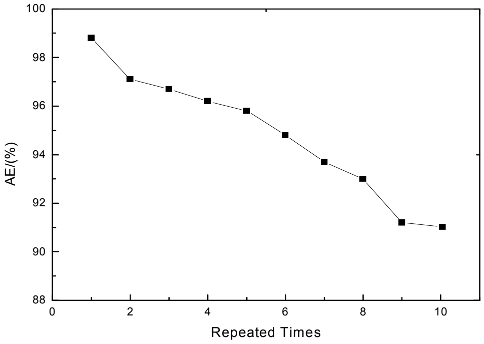

Fig.12 Effect of the cycles on absorption

(experimental conditions: flow rate of gas *G*= 400ml/min; amount of EDA/SiO_2 0.4g in 40mL water; absorption temperature *t*=60 °C; pH=6.0~6.5; concentration of SO_2 C=3000mg/m^3).

As shown in Figure 13, the desorption efficiency of SO_2 increases with the number of cycles raises. The reason is that SO_2 accumulated in the loaded solution during the absorption cycle experiment, and the initial SO_2 concentration increases with the raise of the number of cycles.

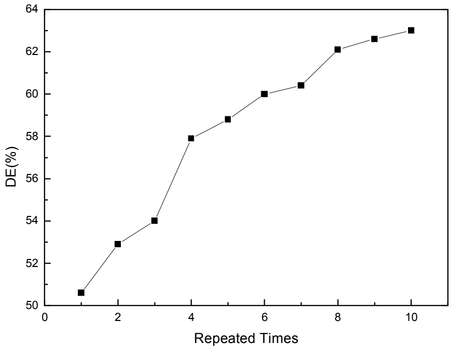

Fig.13 Effect of the cycles on desorption

(experimental conditions: initial concentration of SO_2 in the loaded solution *w*=1.8g/L; amount of EDA/SiO_2 *A*=0.4g in 40mL water; preheating temperature *t* =70 °C; initial pH of the loaded solution pH=5)

5 Conclusions

This paper presented a novel FGD process in which an EDA/SiO_2 - phosphoric acid system was used to absorb sulfur dioxide in the flue gas.

(1) EDA/SiO_2 was prepared. With additive of phosphoric acid, an EDA/SiO_2- phosphoric acid system established which can be used to removal of SO_2 from flue gas.

(2) Using an EDA/SiO_2-phosphoric acid solution as the absorbent, technical conditions in absorption and desorption were experimentally researched. The optimum conditions for absorption were as follows: the amount of EDA/SiO_2 was 0.4g in 40mL water, the preheat temperature was 60℃, the flow rate of gas was 400ml/min, the concentration of SO_2 was 3000mg/m^3 in flue gas, the adsorption time is 60 minutes and the pH was between 6.0 and 6.5. Under the optimum conditions, the absorption efficiency for SO_2 was more than 98%.

(3) The optimal conditions for desorption were as follows: temperature was 70℃, the original pH value of loaded solution was 5, the amount of EDA/SiO_2 was 0.4g in 40mL water and the desorption time is 60min. Under these conditions, the desorption efficiency of loaded solution was more than 50%.

(4) The prepared EDA/SiO_2 as desulfurization agent had many advantages. The mechanical properties of silicone are good, grafted EDA make the specific surface area bigger and adsorption performance better. It was solid, so it solved the problem of traditional desulfurization agent loss. So EDA/SiO_2 material should be better reused in the flue gas desulfurization.

Acknowledgements

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Flue gas desulfurization by immobilized amine is a new desulfurization technique. The EDA/SiO$_2$ and the additive H$_3$PO$_4$ were used as desulphur absorber. SO$_2$ was absorbed by the system and desorbed from the loaded solution. And the cycle operation was also analyzed in the experiments. Some technology conditions such as the amount of EDA/SiO$_2$, the temperature, concentration of SO$_2$ and pH value were experimentally researched. With the optimized process, the absorption efficiency of this system could reach 98% and the desorption efficiency was over 50%, showing good absorption/desorption capability and promising potential to be applied in desulphur area.