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Study on The Selective Absorption of Hydrogen Sulfide From Coal Gas with High Gravity Technology

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The coal gas of hydrogen sulphide (H_2S) containing carbon dioxide (CO_2) is absorbed by alkaline solution in industry. A large number of CO_2 absorption will cause high alkali consumption, side reactions and larger regeneration system. The effect of high gravity factor, liquid-gas ratio, Na_2CO_3 concentration and gas-liquid contact time at the desulfurization rate and selectivity in RPB is investigated in experiment. At the same time, selective desulfurization experiment is compared RPB and packed columns. The results show that the desulfurization rate is 95% and the selectivity is 40 under the condition of high gravity of 95, a liquid-gas ratio of $19L \cdot m^{-3}$, Na_2CO_3 concentration of $12g \cdot L^{-1}$ and gas-liquid contact time of 0.1s in RPB. It can achieve high selective absorption of H_2S and a small amount of CO_2 absorption in RPB, but the selective absorption in the tower packed is poor.

1. Introduction

Coal gas is one of the most important primary energy sources for humanity. The treated and purified gas can be used as civil, industrial fuels and produced chemical products. However, unpurified gas contains a small amount of H_2S gas (about 0.05%), which can corrode equipment and piping. Its direct discharge will cause air pollution(Da Silva Neto.2016). At present, the absorbent of H_2S absorption mainly contains alcohol amine solution(Amararene et al.,.2017; Yih et al.,.2010), carbonate solution(Zhang et al.,.2006), hydrophilic ion-rich adsorbent(Cosoli et al.,.2008) and biological desulfurization bacteria(Kobayashi et al.,.2011). Among them, the desulfurization liquid composed of carbonate and desulfurization catalyst has the advantages of high desulfurization rate and reproducibility, which is a high-performance absorbent. The acid gas in the coal gas contains CO_2 gas (about 3%) in addition to H_2S.When the alkali solution absorbs H_2S gas, it also absorbs a certain amount of CO_2, which seriously affects the quality of the desulfurization solution and brings about many side reactions. Therefore, there is a certain industrial significance for the selective absorption of H_2S in gas.

From the analysis of reaction kinetics, the absorption mechanism of CO_2 is slower than that of H_2S due to the difference in the reaction mechanism between the two gases and the lye, which constitutes the theoretical basis for the selective absorption of H_2S.Many scholars have studied the reaction rate of H_2S, CO_2 and alcohol amine solutions. Yu Weichung(Yu et al.,.1987) measured the reaction rate of MDEA (methyldiethanolamine) with H_2S, CO_2 at normal temperature. The results showed that the two reaction rates differ greatly. The reaction rate of alkali with H_2S, CO_2 is not reported on the literature. The common reaction rate constants are measured by spectroscopy method(Balakhnina et al.,.2017), conductivity method(Tagami et al.,.1974) and spectral electrochemical method(Mozo et al.,.2011) . The conductivity method is simple and high accuracy of the system stability, so conductance method was used to detect the reaction rate constant of alkali solution and H_2S and CO_2 in this paper.

Even if the reaction rate between H_2S, CO_2 and carbonate solution is quite different, long gas-liquid contact time is likely to cause both to absorb all. Therefore, gas-liquid contact time is an important indicator of selective desulfurization. Using the traditional desulfurization tower for selective absorption of H_2S, the residence time of gas-liquid phase is 9s(Yintang et al.,.2004). The absorption rate of CO_2 is more than 10% in this process. Tower equipment is difficult to achieve selective desulfurization. Short residence time and high mass transfer efficiency are important operating parameters for selective absorption. The Rotating Packed

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Bed (RPB)(Lin et al.,.2016) is a transfer device that can strengthen the process. RPB has been widely used in absorption(Sun et al.,.2017), desorption(Tan et al.,.2008), extraction(Modak et al.,.2016), distillation(Sudhoff et al.,.2015). Compared with the traditional tower, RPB has the advantages of short gas-liquid contact time and high mass transfer efficiency, which is an ideal selective absorption device. Haikui Zou(Zou et al.,.2017) used sodium carbonate to absorb H_2S in RPB. The results showed that RPB had a higher removal rate than the packed column. It is an efficient gas-liquid contactor with a greater potential to remove H_2S.
In the experiment, selective absorption performance of simulated coal gas was compared between packed tower and RPB. The effects of gas-liquid contact time, parameters of high gravity factor, liquid-gas ratio and alkali content on desulfurization rate and selectivity were examined in RPB. It gets the best operating conditions in RPB.

2. Experiment

2.1 Experimental mechanism

The miain reaction of selective absorption of H_2S using Na_2CO_3 as a lye is as follows:

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3 \quad (1)$$

$$CO_2 + H_2O + Na_2CO_3 \rightarrow 2NaHCO_3 \quad (2)$$

It can be seen that the reaction of H_2S, CO_2 and Na_2CO_3 was essentially different in the absorption process from above reaction. The reaction between H_2S and alkali was a fast reaction, which was controlled by gas film. The reaction of CO_2 with lye first occured hydration reaction, and then reacted with alkali, which was a pseudo first-order reaction and belongs to liquid film control.

2.2 Selective desulfurization experiments

Experiment was carried out at 0.1Pa and 25 ℃The simulated coal gas consisted of H_2S (0.05%), CO_2 (3%) and N_2 (96.95%). Selective desulfurization equipment used the packed column and RPB as an absorption device. Equipment parameters were shown in Table 1. The absorption solution was sodium carbonate added to the desulfurization catalyst was PDS (binuclear cobalt phthalocyanine ammonium sulfonate).

Table 1.The parameters of RPB and packed column

	RPB	Packed column
Packing type	Stainless steel wire mesh	Stainless steel wire mesh
Packing diameter(mm)	120	90
Packing height(mm)	80	1000
Packing surface area($m^2 \cdot m^{-3}$)	700	2200
Gas flow ($m^3 \cdot h^{-1}$)	0-10	0-10

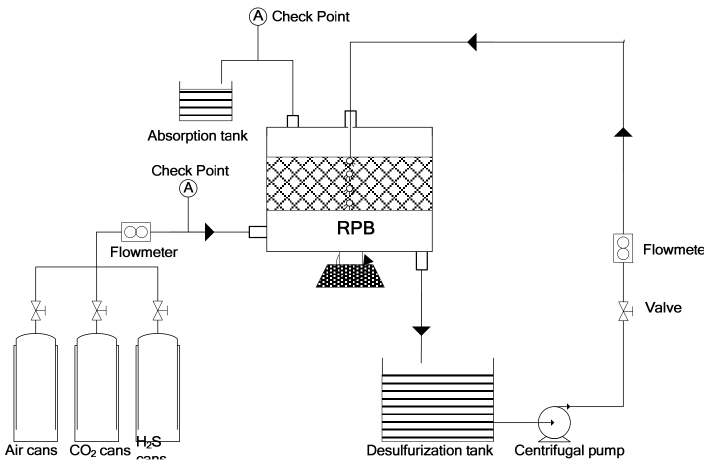

Figure 1: The experimental flow chart of selective absorption of H_2S

Figure 1 shows the experimental process device for selective absorption of H_2S in RPB. The entire packing is connected to the motor and the speed of RPB is changed by controlling the frequency converter. The simulated gas enters RPB from the gas delivery pipe through the rotor flow meter and passes through rotating packing layer from bottom to top. The absorption fluid delivered by the infusion pump enters the inner rim of the packing rotor along the inlet tube and passes radially through the packing. The selective absorption of H_2S is completed under high turbulence, liquid-liquid contact and high-speed interface renewal in RPBImport and export gas concentration detected by gas chromatography (HP-6890, United States Hewlett-Packard).

The calculation method of high gravity factor is expressed by the following equation. The high gravity factor maintained at 40-100 in the experiment.

$$\beta = \frac{\omega^2 r}{g} \tag{3}$$

where ω is the rotor angular velocity (s^{-1}), r is the radius of filler rotor (m), N is the rotation speed of rotor ($r \cdot min^{-1}$).

Gas-liquid contact time in RPB is calculated by the following equation. The research scope of gas-liquid contact time is 0-1.6s.

$$\mu = \frac{Q}{\pi H\left(r_2^2 - r_1^2\right)} \tag{4}$$

where Q is gas flow rate ($m^3 \cdot h^{-1}$), H is the axial height (m), r_1 and r_2 are the inner and outer diameter (m).

The liquid velocity is greatly affected by the structure of equipment in RPB. In this experiment, liquid spray density is used to study the absorption performance instead of liquid flow rate. The expression is shown in the following equation.

$$q = \frac{L}{2\overline{r}\pi H} \tag{5}$$

where L is the liquid flow rate ($L \cdot h^{-1}$), $\overline{r}$ is the average radius of filler (m).

In the experiment, the purifying effect of the gas is characterized by the desulfurization rate (E_{H_2S}) and the decarburization rate (E_{CO_2}). They are expressed by the following equation.

$$E_{H_2S} = \left(c_{in,H_2S} - c_{out,H_2S}\right) \times 100\% / c_{in,H_2S} \tag{6}$$

$$E_{CO_2} = \left(c_{in,CO_2} - c_{out,CO_2}\right) \times 100\% / c_{in,CO_2} \tag{7}$$

where c_{in,H_2S} and c_{out,H_2S} are inlet and outlet H_2S concentration, c_{in,CO_2} and c_{out,CO_2} are inlet and outlet CO_2 concentration.

Desulfurization selectivity (S) indicates selective desulfurization effect. Its expression is expressed by the following equation.

$$S = E_{H_2S} / E_{CO_2} \tag{8}$$

3. Results and discussion

3.1 Determination of reaction rate constant

The reaction rate constants of H_2S, CO_2 and Na_2CO_3 are 2.1×10^{-1} $min^{-1}\cdot mol^{-1}\cdot L$, 4.1×10^{-4} $min^{-1}\cdot mol^{-1}\cdot L$. The reaction rate between H_2S and Na_2CO_3 is about 500 times that of CO_2. This difference in absorption constitutes the chemical basis for the selective absorption of H_2S. This difference makes the two acid gases react with Na_2CO_3 at the same time, it can achieve selective absorption as long as the control of the gas-liquid contact time.

3.2 Selective tower desulfurization experiment

Figure 2 shows the effect of spray density on the desulfurization rate and selectivity in the packed tower under conditions of Na_2CO_3 solution concentration of 12 $g \cdot L^{-1}$ and gas velocity of $3m^3 \cdot h^{-1}$. It can be seen from the figure that the desulfurization rate of H_2S increases with the increase of spray density, and the selectivity decreases with the increase of spray density. When the spray density is more than 1.5 $m^3 \cdot (m^{-2} \cdot h^{-1})$, the desulfurization rate can be maintained above 90% and meet the requirements within the appropriate liquid load range. However, the selectivity factor is only 1-2. This is due to adequate gas-liquid contact and increase gas-liquid contact time within a certain range of static packing height. Alkali also causes a lot of CO_2 absorption. The selective effect is not obvious.

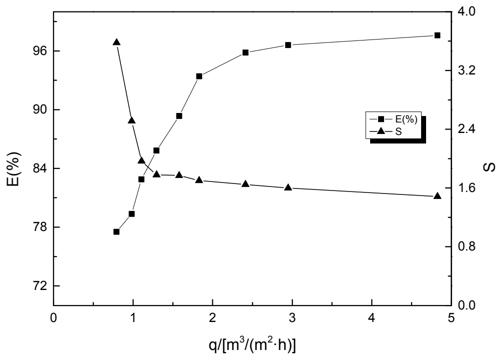

Figure 2: Effect of spray density in packed tower desulfurization between RPB and packed tower

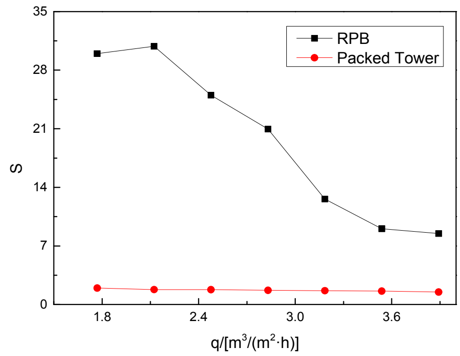

Figure 3: Selective comparison of on desulfurization rate and selectivity

3.3 Experimental Comparison of Desulfurization in RPB and Packed Tower

Selective absorption performance of packed column and RPB is compared at gas velocity of 3 $m^3 \cdot h^{-1}$, high gravity factor is 90, inlet H_2S and CO_2 concentrations of 1600 ppm and 14000 ppm respectively, and the same liquid spray density. Figure 3 shows that the packing column has a selectivity of one-twentieth RPB at the same liquid spray density. This shows that the packed column has poor selectivity and no superiority in the selective desulfurization process.

3.4 RPB selective desulfurization experiment

3.4.1 Influence of high gravity factor on desulfurization rate and selectivity

Figure 4 shows the effect of the high gravity factor on the desulfurization rate and selectivity at a constant gas velocity of $2.8m^3 \cdot h^{-1}$, a liquid velocity of $56L \cdot h^{-1}$, and the inlet H_2S and CO_2 concentrations are 1777 ppm and 13500 ppm respectively.

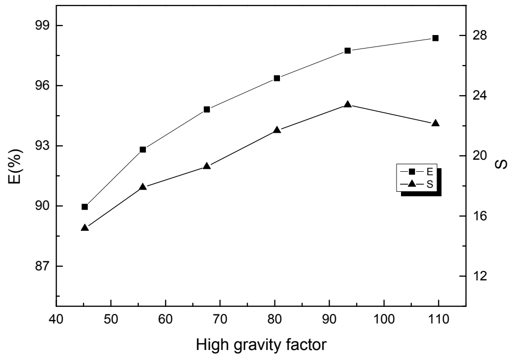

Figure 4: Effect of high gravity factor on desulfurization rate and selectivity

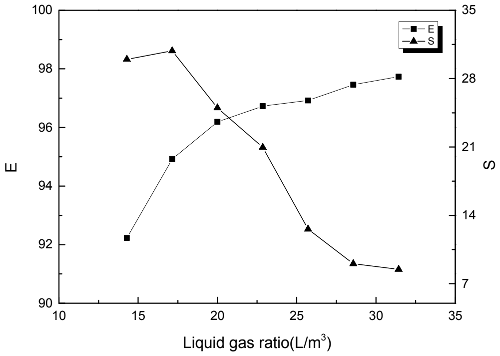

Figure 5: Effect of liquid-gas ratio on desulfurization rate and selectivity

The desulfurization rate increases as the increase of the high gravity factor. When the high gravity factor reaches 90, the desulfurization rate is no longer increasing obviously with the increase of the high gravity factor, and the desulfurization rate reaches more than 97%. The increase of the high gravity factor enhances the effect of mass transfer between gas and liquid. The liquid droplet is cut into liquid silk and liquid film, which indirectly increases the gas-liquid contact area. Experiments also showed that The tendency of selective presentation to rise first and then decrease increases with the high gravity factor. When the high gravity factor is 94, the selectivity is highest. It can see that the size on the desulfurization rate has a great influence on the selectivity by the selective expression. When the high gravity factor increases, the desulfurization rate and the desulfurization rate increase at the same time. However, when the high gravity factor is greater than 94, the desulfurization rate increases more than the desulfurization rate. It results in the decrease of selectivity for desulfurization.

3.4.2 Effect of Liquid - Gas Ratio on Desulfurization Rate and Selectivity

Figure 5 shows the effect of liquid-gas ratio on desulfurization rate and selectivity at a constant gas velocity of $2.8m^3 \cdot h^{-1}$, a high gravity factor of 94, and H_2S and CO_2 concentration of 1712 ppm and 13000 ppm respectively. In the case of gas remains unchanged, the liquid velocity changes to change the liquid-gas ratio throughout the process.

The desulfurization rate increases and the selectivity decreases as the liquid-gas ration increases. The large liquid-gas ratio causes an increase in the amount of gas absorbed per unit velocity of gas and increases the chance of contact between the gas-liquid two-phase, which in turn causes the acid gas to fully react with the caustic. Due to the different reaction rates of H_2S and CO_2 with Na_2CO_3, the absorption of H_2S reaches the limit and the absorption of CO_2 increases slowly during the absorption process, so that the desulfurization selectivity decreases. Experiment meets the qualified desulfurization rate cases, but also to meet the high selectivity. So the liquid-gas ratio should be controlled at 20L·m^{-3} under experimental conditions.

Removal of H_2S by RPB can enhance gas-liquid mass transfer(Qi et al.,.2011). In the packed column(Hatsugai et al.,.2011), the desulfurization rate reaches 90% when the liquid-gas ratio is 110 L·m^{-3}, which is 100 times that of RPB. Low liquid-gas ratio is conducive to reducing circulation and retention, saving energy. At the same time, lower liquid-gas ratio can increase its selectivity.

3.4.3 Effect of Alkali concentration on Desulfurization Rate and Selectivity

Fig 6 shows the effect of Na_2CO_3 concentration on desulfurization rate and selectivity at a constant gas velocity of 2.8 m^3·h^{-1}, a high gravity factor of 94, H_2S and CO_2 concentrations of 1053 ppm and 12500 ppm respectively.

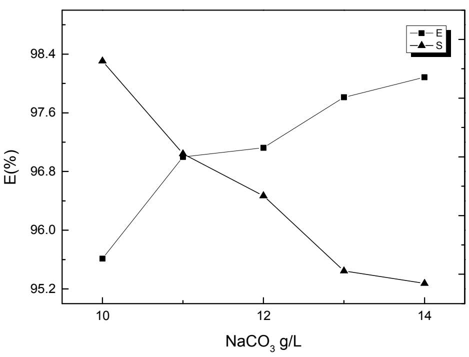

Figure 6: Effect of alkali concentration on selectivity

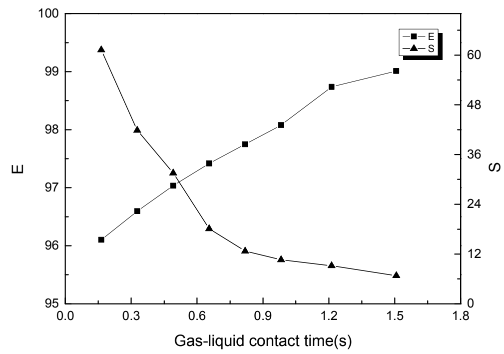

Figure 7: Effect of gas-liquid contact time on desulfurization rate and selectivity

The desulfurization rate rises slowly and the selectivity decreases significantly with Na_2CO_3 concentration increasing from 10 g·L^{-1} to 14 g·L^{-1}. It shows that the higher the concentration of Na_2CO_3, the better the effect of removing H_2S, but it will accelerate the reaction of Na_2CO_3 and CO_2 at the same time. The high concentration of Na_2CO_3 accelerates the side reactions and reduces the quality of the desulfurization solution. Although low concentration of Na_2CO_3 guarantees higher selectivity, it is less effective in removing H_2S. Therefore, the concentration of Na_2CO_3 is selected to be 12 g·L^{-1} in this experiment, which not only guarantees a higher desulfurization effect, but also does not cause a poor selectivity due to a low selectivity.

3.4.4 Influence of gas-liquid contact time on desulfurization rate and selectivity

Fig 7 shows the effect of gas-liquid contact time on desulfurization rate and selectivity at H_2S and CO_2 concentrations of 1200 ppm and 13000 ppm respectively, a high gravity factor of 94. Gas-liquid contact time is achieved by changing the gas flow rate.

The experimental results show that the desulfurization rate has an increasing trend in the increase of gas-liquid contact time. This is because the long gas-liquid contact time makes gas-liquid contact more fully. When the gas-liquid contact time is less than 0.2 s, the desulfurization rate can still reach more than 95% in RPB. The RPB is a device that can enhance mass transfer. Mass transfer can reach higher levels of RPB in a short period of time. However, the downward trend of selectivity is obviously with increasing gas-liquid contact time. As the alkali to CO_2 absorption increases and H_2S absorption reaches a certain limit, which in turn led to a decline in selectivity. Gas-liquid contact time is an important reference for the selective absorption of H_2S. The gas-liquid contact time in RPB is significantly less than the traditional tower equipment for tens of seconds. RPB is very suitable for selective absorption system. In the selective desulfurization process, RPB has more technical advantages than the packed tower.

4. Conclusions

This work investigates the selective removal of H_2S from coal gas in the RPB. The experimental method of H_2S removal is wet oxidation, in which the desulfurizer consists of Na_2CO_3 (12g·L^{-1}) and PDS catalysts (0.13 mol·L^{-1}), and H_2S, CO_2 are simulated according to the actual ratio of coal gas. In addition, the effects of high gravity factor, liquid-gas ratio, Na_2CO_3 concentration and gas-liquid contact time on desulfurization rate and selectivity in RPB were investigated. The desulfurization rate increases with the increase of high gravity factor, liquid-gas ratio, Na_2CO_3 concentration and gas-liquid contact time. The selectivity increases first and then decreases with the increase of high gravity factor, and it decreases with the increase of liquid-gas ratio, Na_2CO_3 concentration and gas-liquid contact time. The desulfurization rate can reach over 95% and the selectivity factor is 40 at liquid-gas ration of 20 $L \cdot m^{-3}$ in the RPB. When the desulfurization rate reaches 90%, the selectivity factor is only 1-2 in the packed tower and it does not meet the requirements on the choice of desulfurization. Experiment shows that the RPB is feasible for selective desulfurization of coal gas, which has the advantages of short gas-liquid contact time, high desulfurization rate and selectivity compared with packed tower.

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References

Da Silva Neto, O.G., De Freitas, Christian Alberto Lopes Burrone (2016) Study of dispersing hydrogen sulfide (H_2S) generated from a chemical industry, Chemical Engineering Transactions 54: 235- 240.

Amararene, F., Bouallou, C. (2017) Study of hydrogen sulfide absorption with diethanolamine in methanolic aqueous solutions, Chemical Engineering Transactions 52.

Balakhnina, I.A., Brandt, N.N., Mankova, A.A., et al. (2017) Raman Spectral Determination of Chemical Reaction Rate Characteristics, Journal of Applied Spectroscopy: 1-7.

Cosoli, P., Ferrone, M., Pricl, S., et al. (2008) Hydrogen sulfide removal from biogas by zeolite adsorption. Part II. MD simulations, Chemical Engineering Journal 145: 93-99.

Da Silva Neto, O.G., De Freitas, Christian Alberto Lopes Burrone (2016) Study of dispersing hydrogen sulfide (H_2S) generated from a chemical industry, Chemical Engineering Transactions 54: 235- 240.

Hatsugai, T., Kikano, M.andSato, K. (2011) A Study of Hydrogen Sulfide Absorption in a Packed Tower, Kagaku Kogaku Ronbunshu 37: 156-161.

Kobayashi, T., Li, Y.Y., Kubota, K., et al. (2011) Environmental and Microbial Ecology in Sulfur Mats Responsible for the Biological Removal of Hydrogen Sulfide from Biogas, J.env.cons.eng 38: 642-651.

Lin, C.C., Tsai, C.H. (2016) Micromixing in a rotating packed bed with blade packings, Journal of the Taiwan Institute of Chemical Engineers 63: 33-38.

Modak, J.B., Bhowal, A.andDatta, S. (2016) Extraction of dye from aqueous solution in rotating packed bed, Journal of Hazardous Materials 304: 337-342.

Mozo, J.D., Carbajo, J., Sturm, J.C., et al. (2011) The use of digital simulation to improve the cyclic voltammetric determination of rate constants for homogeneous chemical reactions following charge transfers, Analytica Chimica Acta 699: 33-43.

Qi, G.S., Liu, Y.Z.andJiao, W.Z. (2011) Study on Industrial Application of Hydrogen Sulfide Removal by Wet Oxidation Method with High Gravity Technology, China Petroleum Processing & Petrochemical Technology 13: 29-34.

Sudhoff, D., Leimbrink, M., Schleinitz, M., et al. (2015) Modelling, design and flexibility analysis of rotating packed beds for distillation, Chemical Engineering Research & Design 94: 72-89.

Sun, B.C., Sheng, M.P., Gao, W.L., et al. (2017) Absorption of Nitrogen Oxides into Sodium Hydroxide Solution in a Rotating Packed Bed with Preoxidation by Ozone, Energy & Fuels 31: 11019-11025.

Tagami, S., Matsuba, A., Sawada, T., et al. (1974) [Studies on chemical analysis by measurement of reaction rate. II. Conductivity method for determination of urea by using urease (author's transl)], Yakugaku Zasshi Journal of the Pharmaceutical Society of Japan 94: 1384-1388.

Tan, C.S., Lee, P.L. (2008) Supercritical CO_2 desorption of activated carbon loaded with 2,2,3,3-tetrafluoro-1-propanol in a rotating packed bed, Environmental Science & Technology 42: 2150-2154.

Yih, S.M., Sun, C.C. (2010) Simultaneous Absorption of Hydrogen Sulfide and Carbon Dioxide into di-isopropanolamine Solution, Canadian Journal of Chemical Engineering 65: 581-585.

Yintang, L., Tao, T.andJun, L. (2004) Residence time of droplets in a spray scrubber for FGD, Techniques and Equipment for Environmental Pollution Control 5: 89-91.

Yu, W.C., Astarita, G. (1987) Design of packed towers for selective chemical absorption, Chemical Engineering Science 42: 425-433.

Zhang, Y., Wang, X.Q., Ning, P., et al. (2006) Study on the Absorption of Hydrogen Sulfide by Sodium Carbonate Solution, Yunnan Chemical Technology.

Zou, H.K., Sheng, M.P., Sun, X.F., et al. (2017) Removal of hydrogen sulfide from coke oven gas by catalytic oxidative absorption in a rotating packed bed, Fuel 204: 47-53.