Study of a mass transfer-reaction model for SO₂ absorption process using LAS/H₂SO₄ solution

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Abstract: A regenerative absorption process for removal of SO_x from FCC off-gas using LAS/H₂SO₄ solution as absorbant was studied and pilot-plant experiments were carried out. A mass transfer-reaction model for the SO₂ absorption process was established based on pilot-plant experiments, and the concentration distribution of components in the liquid film, and the partial pressure and mass transfer rate of SO₂ along the height of the absorption tower, was calculated from this model. The numerical simulation results were compared with the experimental results and proved that the model can be used for describing the SO₂ absorption process.

Key words: Regenerative absorption process, SO_x cleanup, LAS/H₂SO₄ solution, mass transfer-reaction model

1 Introduction

SO_x emissions from coal combustion, oil combustion and oil refining are increasing along with the increasing demand for energy. SO_x is one of the main air pollutants, and seriously endangers the environment by forming acid rain and so on. Control of SO_x emissions is important to protect the environment and reduce air pollution, and it has received extensive attention at home and abroad (Cheng, 1999; Hao et al, 2000; 2001; Robert, 2001; Srivastava et al, 2001; Xiao and Wu, 2001).

A regenerative absorption process for SO_x cleanup using LAS/H₂SO₄ solution as absorbent was developed by the Luoyang Petrochemical Engineering Corporation (Liu, 2002; Qi et al, 2003). It has the advantages of low equipment requirements, easy operation, low running cost and high desulfurizing efficiency without secondary pollution.

The regenerative absorption process deals with a multicomponent mixture and includes the mass transfer and reaction of components between gas and liquid phases. To model such a process, knowledge of multicomponent diffusion and reaction kinetics is necessary. The rate-based model based on the two-film mass transfer theory has been widely used to describe multicomponent chemical absorption processes (Cooper et al, 1997; Ebrahimia et al, 2003; Manoj et al, 2001; Takashina et al, 2001).

The pilot-plant experiments were carried out in the fluid catalytic cracking unit (FCC) of the Luoyang Refinery.

Based on the results, a model for SO₂ mass transfer and absorption reaction process was established using the two-film mass transfer theory and the concentration distribution of components in the liquid film, and partial pressure and mass transfer rate of SO₂ along the column height of the absorption tower, was calculated from this model.

2 Experimental investigation

The pilot-plant experimental apparatus is composed of water scrubber, absorption, regeneration and resin towers, as shown in Fig. 1, and the experimental conditions are shown in Table 1.

The hot FCC off-gas (with a temperature of 160-180 °C and a SO₂ content of 1,000-2,000 mg/m³) was sent to the bottom of water scrubber tower to remove the catalyst dust and strong acidic gas, and cooled to 45 °C. The cooled off-gas was then sent to the absorption tower where the gas was countercurrently contacted with the LAS/H₂SO₄ solution and the SO₂ was absorbed by LAS/H₂SO₄ solution. Part of the SO₂-rich LAS/H₂SO₄ solution was pumped to the absorption tower for recycling, the remaining part was pumped to the regeneration tower, via a lean/rich solution heat exchanger for energy recovery, and the LAS/H₂SO₄ solution was regenerated by indirect steam stripping when SO₂ was recovered as a pure, water-saturated product from the SO₂ rich LAS/H₂SO₄ solution. During the absorption-desorption process, a small amount of SO₂ was converted to SO₃ due to oxidization and existed in the LAS/H₂SO₄ solution as heat stable sulfate. In order to maintain the ion balance of SO₄²⁻ in the absorption-regeneration system, a small part of lean

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solution from the regeneration tower was pumped to the resin tower to remove the heat stable salts. The by-product SO_2 can be converted to various sulfur products such as liquid SO_2 , sulfuric acid or sulfur.

Fig. 1 The experimental devices for SO_2 absorption process

Table 1 The main experimental equipments and the experimental conditions

Equipment	Experimental conditions
Water scrubber (empty tower)	Flue gas flow: $50 \text{ Nm}^3/\text{h}$ Flue gas flow rate: 1 m/s Flue gas inlet temperature: $160\text{--}180^\circ\text{C}$ Flue gas exit temperature: $<50^\circ\text{C}$
Absorption tower (packed column) (dixon ring of $\phi 6\text{mm} \times 6\text{mm}$)	Flue gas flow rate: 1 m/s Residence time: 0.6 s Flue gas exit temperature: around 50°C Spray volume: 50 kg/h Liquid-to-gas ratio: $0.2\text{--}0.5 \text{ kg/m}^3$ Absorbing solution inlet temperature: 45°C Absorbing solution exit temperature: 50°C Concentration of absorbing solution: 1 mol/L
Regeneration tower (packed column) (dixon ring of $\phi 6\text{mm} \times 6\text{mm}$)	Regeneration amount: $10\text{--}25 \text{ kg/h}$ rich solution Top temperature: 100°C Bottom temperature: $<120^\circ\text{C}$ Regeneration time: 2 h
Resin tower (D301 resin)	Ion-exchange temperature: 40°C Handling amount: $<1\%$ lean solution Air speed: 0.5 h^{-1}

To determine the gaseous partial pressure of SO_2 at the top, middle and bottom of the absorption tower, a LC-2 microcoulometer was used. The furnace temperature was 500°C and exit temperature was 850°C . The temperature of gasification zone was 60°C . The flow rates of air, nitrogen and sample gas were 40 ml/min , 160 ml/min and 30 ml/min , respectively.

3 Mass transfer-reaction model for SO_2 absorption process

It is assumed that the absorption tower was operated under adiabatic steady-state conditions and the gas-liquid two-phase flow was the plug flow. Chemical reactions occurred in the SO_2 absorption process are as follows:

The above reactions are rapid chemical reactions except reaction (4). R in reactions (6) and (7) represents the absorbent LAS.

3.1 Material balances in the absorption tower

3.1.1 For the gas phase

On the infinitesimal cross-section dz of the absorption tower, SO_2 material balances in gas phase is given by

$$\frac{G}{RTS} \frac{dp_{\text{SO}_2,b}}{dz} = -N_{\text{SO}_2,b}^g a_w \quad (10)$$

where G is the gas liquid, m^3/s ; R is the gas constant, $8.314 \text{ J}/(\text{mol} \cdot \text{K})$; T is the temperature, K ; S is the cross-section area of the tower, m^2 ; $p_{\text{SO}_2,b}$ is the partial pressure of SO_2 , Pa ; a_w is the wet specific interfacial area of the filling, m^2/m^3 ; $N_{\text{SO}_2,b}^g$ is the molar flux of SO_2 through the gas-liquid interface, $\text{mol}/(\text{m}^2 \cdot \text{s})$; z is the transverse coordinate directed from the gas phase to the liquid phase, m .

3.1.2 For the liquid phase

On the infinitesimal cross-section dz of the absorption tower, the material balance of component A ($\text{SO}_{2(\text{aq})}$, HSO_3^- , SO_3^{2-} , HSO_4^- , SO_4^{2-} , RH^+ , RH_2^{2+} , H^+ , OH^-) in liquid phase is shown as the following equation

$$N_{A,b}^l a_w + R_{A,b}^l \varepsilon_l = \frac{L}{S} \frac{dC_{A,b}}{dz} \quad (11)$$

where L is the liquid flow, L/h ; $C_{A,b}$ is the concentration of A in liquid, mol/L ; $N_{A,b}^l$ is the molar flux of A through the gas-liquid interface, $\text{mol}/(\text{m}^2 \cdot \text{s})$; $R_{A,b}^l$ is the reaction rate of component A, $\text{mol}/(\text{L} \cdot \text{s})$; ε_l is the liquid holdup, m^3/m^3 .

3.1.3 Combining the gas and liquid phases

The mass balance for all sulfur components is established by combining the sulfur components material balance equations of gas and liquid phases. The total sulfur components flux in the liquid film is a constant and it is equivalent to the SO_2 flux in the gas phase. The total sulfur component equation in the liquid phase becomes

$$\frac{L}{S} \frac{dC_{\text{S-total,b}}}{dz} = N_{\text{SO}_2,i}^g a_w \quad (12)$$

This is the SO_2 flux equation, and it is related to SO_2

concentration gradient on the interface between the gas and liquid. So, it is important to know the SO_2 concentration profile and mass balance equations of different components in the liquid film.

3.2 Diffusion and reaction equations of components in the liquid film

Because chemical reactions occur in the liquid film (i.e. liquid phase), the molar flux along the x direction of the coordinate system for each component in gas phase is a constant (Kenig, 1995 and 2000; Kenig and Gorak, 1995; Kenig et al, 1999 and 2001). Equation (13) is used to describe the diffusion process in the gas phase.

$$\frac{dN_A^g}{dx} = 0 \quad (13)$$

The equation used to describe the diffusion and reaction process in the liquid phase is as follows

$$\frac{dN_A^l}{dx} = R_A \quad (14)$$

where R_A is the reaction rate constant of component A, mol/(L·s). The diffusion flux of each component can be written as follows

$$N_A = -D_A \frac{dC_A}{dx} \quad (15)$$

where D_A is the diffusion coefficient of component A, m^2/s ; C_A is the molar concentration of component A, mol/L.

By substituting Equation (15) into Equation (14), and combining the material balance of each component (H_2SO_3 , HSO_3^- , SO_3^{2-} , HSO_4^- , SO_4^{2-} , RH^+ , RH_2^{2+} , H^+ , OH^-), the total sulfur balance equation can be described as follows

$$D_{\text{SO}_2} \frac{d^2 C_{\text{SO}_2}}{dx^2} + D_{\text{HSO}_3^-} \frac{d^2 C_{\text{HSO}_3^-}}{dx^2} + D_{\text{SO}_3^{2-}} \frac{d^2 C_{\text{SO}_3^{2-}}}{dx^2} + D_{\text{HSO}_4^-} \frac{d^2 C_{\text{HSO}_4^-}}{dx^2} + D_{\text{SO}_4^{2-}} \frac{d^2 C_{\text{SO}_4^{2-}}}{dx^2} = 0 \quad (16)$$

The effect of the gradient of electric potential difference on the ion flux can be neglected, so the charge flux equation in the liquid film becomes

$$D_{\text{H}^+} \frac{dC_{\text{H}^+}}{dx} + D_{\text{RH}^+} \frac{dC_{\text{RH}^+}}{dx} + 2D_{\text{RH}_2^{2+}} \frac{dC_{\text{RH}_2^{2+}}}{dx} - D_{\text{HSO}_3^-} \frac{dC_{\text{HSO}_3^-}}{dx} - 2D_{\text{SO}_3^{2-}} \frac{dC_{\text{SO}_3^{2-}}}{dx} - D_{\text{HSO}_4^-} \frac{dC_{\text{HSO}_4^-}}{dx} - 2D_{\text{SO}_4^{2-}} \frac{dC_{\text{SO}_4^{2-}}}{dx} - D_{\text{OH}^-} \frac{dC_{\text{OH}^-}}{dx} = 0 \quad (17)$$

As mentioned above, chemical reaction equations (2)-(3) and (5)-(9) in the liquid film could reach equilibrium rapidly, so the chemical equilibrium equations for chemical reactions (2)-(3) and (5)-(9) can be established as Equations (18)-(24), respectively. The values of ionization equilibrium constants are shown in Table 2.

$$K_{s1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} \quad (18)$$

$$K_{s2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} \quad (19)$$

$$K_w = [\text{H}^+][\text{OH}^-] \quad (20)$$

$$K_{\text{LAS}_1} = \frac{[\text{RH}^+][\text{OH}^-]}{[\text{R}]} \quad (21)$$

$$K_{\text{LAS}_2} = \frac{[\text{RH}_2^{2+}][\text{OH}^-]}{[\text{RH}^+]} \quad (22)$$

$$K_{\text{H}_2\text{SO}_4^1} = \frac{[\text{H}^+][\text{HSO}_4^-]}{[\text{H}_2\text{SO}_4]} \quad (23)$$

$$K_{\text{H}_2\text{SO}_4^2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \quad (24)$$

Table 2 The values of ionization equilibrium constant for reactions (2)-(3) and (5)-(9)

Ionization equilibrium constant	Value	Ionization equilibrium constant	Value
K_{s1}	1.7×10^{-2}	$K_{\text{H}_2\text{SO}_4^2}$	1.0×10^{-2}
K_{s2}	6.3×10^{-8}	K_{LAS_1}	1.87×10^{-5}
K_w	1.0×10^{-14}	K_{LAS_2}	3.63×10^{-7}
$K_{\text{H}_2\text{SO}_4^1}$	1.0×10^3		

3.2.1 Interface boundary conditions

The SO_2 absorption rate is equivalent to the total sulfur components flux on the interface between gas and liquid, and it is also equivalent to the SO_2 flux in the gas film. Therefore, Equation (25) can be derived.

$$N_{\text{SO}_2,i}^g a = \frac{k_g}{RT} (p_{\text{SO}_2,b} - p_{\text{SO}_2,i}) = - \left[D_{\text{SO}_2} \frac{dC_{\text{SO}_2}}{dx} \right]_{x=0} + D_{\text{HSO}_3^-} \frac{dC_{\text{HSO}_3^-}}{dx} \bigg|_{x=0} + D_{\text{SO}_3^{2-}} \frac{dC_{\text{SO}_3^{2-}}}{dx} \bigg|_{x=0} + D_{\text{HSO}_4^-} \frac{dC_{\text{HSO}_4^-}}{dx} \bigg|_{x=0} + D_{\text{SO}_4^{2-}} \frac{dC_{\text{SO}_4^{2-}}}{dx} \bigg|_{x=0} \quad (25)$$

where, $p_{\text{SO}_2,i} = H_{\text{SO}_2,i} C_{\text{SO}_2,i}$, $H_{\text{SO}_2,i}$ is Henry's law constant of SO_2 , Pa·L/mol. k_g is the gas phase mass transfer coefficient, m/s. If $x=0$, the net increase of charge flux is equal to zero.

$$D_{\text{H}^+} \frac{dC_{\text{H}^+}}{dx} \bigg|_{x=0} + D_{\text{RH}^+} \frac{dC_{\text{RH}^+}}{dx} \bigg|_{x=0} + 2D_{\text{RH}_2^{2+}} \frac{dC_{\text{RH}_2^{2+}}}{dx} \bigg|_{x=0} - D_{\text{HSO}_3^-} \frac{dC_{\text{HSO}_3^-}}{dx} \bigg|_{x=0} - 2D_{\text{SO}_3^{2-}} \frac{dC_{\text{SO}_3^{2-}}}{dx} \bigg|_{x=0} - D_{\text{HSO}_4^-} \frac{dC_{\text{HSO}_4^-}}{dx} \bigg|_{x=0} - 2D_{\text{SO}_4^{2-}} \frac{dC_{\text{SO}_4^{2-}}}{dx} \bigg|_{x=0} - D_{\text{OH}^-} \frac{dC_{\text{OH}^-}}{dx} \bigg|_{x=0} = 0 \quad (26)$$

3.2.2 Boundary conditions in the liquid phase

In the liquid phase, the mass equations of total sulfur components and total absorbent components, and the charge balance equations, at equilibrium are as follows respectively:

$$C_{\text{total,S}} = C_{\text{H}_2\text{SO}_3,\text{b}} + C_{\text{HSO}_3^-\text{,b}} + C_{\text{HSO}_4^-\text{,b}} + C_{\text{SO}_3^{2-}\text{,b}} + C_{\text{SO}_4^{2-}\text{,b}} \quad (27)$$

$$C_{\text{total,R}} = C_{\text{R}} + C_{\text{RH}^+} + C_{\text{RH}_2^{2+}} = 1 \quad (28)$$

$$C_{\text{H}^+} + C_{\text{RH}^+} + 2C_{\text{RH}_2^{2+}} - C_{\text{HSO}_3^-} - 2C_{\text{SO}_3^{2-}} - C_{\text{HSO}_4^-} - 2C_{\text{SO}_4^{2-}} - C_{\text{OH}^-} = 0 \quad (29)$$

3.3 Model Parameters

Modeling of the SO₂ absorption process in a packed absorption tower is done based on the experimental conditions. The model parameters are shown in Table 3. The liquid-phase diffusion coefficient K_L is obtained with the Nernst-Hartley equation which describes the mass transfer properties (Horvath, 1985). The gas-phase diffusion coefficient K_G is estimated according to the Chapman-Enskog-Wilke-Lee model (Reid et al, 1987). The value of the film thickness δ is usually estimated via the diffusion coefficients and the mass transfer coefficient in the liquid-phase, and thus dependent largely on a number of factors like process hydrodynamics, column geometry, transport and physical properties, etc.

Table 3 The values of parameters for transfer-reaction model

Parameter	Value
Temperature T , K	318
Pressure P , atm	1
Gas flow G , m ³ /h	50
Liquid flow L , L/h	12
P_{SO_2} , atm	0.002
pH	6.8
$C_{\text{H}_2\text{SO}_4}$, mol/L	0.685
Gas phase mass transfer coefficient K_G , m/s	0.0012
Liquid phase mass transfer coefficient K_L , m/s	1.0875×10^{-5}
Height of tower, m	1.8
Filling height, m	1.2
C_{R} , mol/L	1

4 Numerical simulation results

The concentration profiles of components in the liquid film, and the gaseous partial pressure and mass transfer rate of SO₂ along the height of absorption tower can be calculated by combination of the total sulfur balance equation (16), chemical equilibrium equations (18)-(24) and boundary condition equations (25)-(29). The mass transfer-reaction

model consists of matrix-based partial differential and algebraic equations. These equations were solved numerically using Matlab procedures, with a discretization in regard to the column height and film thickness coordinates.

4.1 Concentration profiles in the liquid film

Since chemical reactions occur in the liquid phase only, the component fluxes in the gas phase film region remain constant. Therefore, it is not necessary to discretize the gas phase film. The calculation results of component concentrations and pH in the liquid phase are shown in Figs. 2 and 3, η is the dimensionless film coordinate ($\eta = z/\delta$). In Fig.

Fig. 2 The numerical simulation results of concentration profiles in the liquid film

Fig. 3 The numerical simulation results of pH profile in the liquid film

2, the SO_2 concentration is high in the region near the gas-liquid interface ($\eta=0$), which corresponds to the fast transfer of SO_2 . Because of SO_2 absorption, pH decreases greatly in the region near gas-liquid interface as shown in Fig. 3. The SO_2 concentration is low in the region near the liquid film ($\eta=1$), where the reactions (1)-(9) take place, resulting in an increase in the concentrations of HSO_4^- and SO_4^{2-} . H^+ generated during SO_2 absorption process is consumed in this region, and the pH changes little.

4.2 Partial pressure and mass transfer rate of SO_2 along the height of the absorption tower

The partial pressure and mass transfer rate of SO_2 along the height of the absorption tower are shown in Figs. 4 and 5. The SO_2 gaseous partial pressure reduces from the bottom to the top of the tower, and the mass transfer rate of SO_2 also reduces. The simulation result of SO_2 gaseous partial pressure at the top of tower is in good agreement with the experimental results.

Fig. 4 The numerical simulation results of SO_2 partial pressure along the height of the absorption tower

Fig. 5 The numerical simulation results of mass transfer rate of SO_2 along the height of the column

5 Conclusions

A regenerative absorption process for SO_x cleanup using $\text{LAS}/\text{H}_2\text{SO}_4$ solution as absorbent was developed by the Luoyang Petrochemical Engineering Corporation, and pilot-plant experiments were carried out. Based on the results of the pilot-plant experiments, a model for SO_2 mass transfer and absorption reaction process was established by the two-film mass transfer theory and the concentration distribution of components in the liquid film, partial pressure and mass transfer rate of SO_2 along the column height of the absorption tower, was calculated from this model.

The pilot-plant experimental apparatus is composed of water scrubber, absorption, regeneration and resin towers. The gaseous partial pressure of SO_2 at the top, middle and bottom of the absorption tower was determined.

Modeling of the SO_2 absorption process in a packed absorption tower is done based on the experimental conditions. The model consists of a system of matrix-based partial differential and algebraic equations. These equations have been solved numerically using Matlab procedures, with a discretization in regard to the column height and film thickness coordinates. The numerical solution agreed well with the experimental data. This proved that the model can be reasonably used to describe the SO_2 absorption process.

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