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Modeling and simulation of a wetted-wall column for SO_2 absorption with aqueous ammonia solution

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ABSTRACT

In a wetted-wall column of pilot-scale sulphur dioxide removal efficiencies were measured at 20□ and atmospheric pressure with aqueous ammonia solutions. The liquid-phase mass transfer coefficient and gas-phase mass transfer coefficients of the system were determined. Based on the classical two-film theory the mathematical model was built to describe the complex absorption process. Combined with the valuation of the model parameters and the appropriate boundary conditions the model equations were solved and got the concentration distribution of each component in the liquid film and pH value, gas partial pressure and enhancement factor of distribution along the tower. Compared experimental results with the initial concentration of desulfurization efficiency. The results show that the numerical results were in good agreement with experimental results.

Key words: Kinetics; SO_2 absorption; Wetted-wall column; Mass transport

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INTRODUCTION

It is well known that sulfur dioxide exist in the flue gases of power plants and industrial boilers lead to acid rain which damages buildings, vegetation and water ground cycle [1, 2]. SO_2 is also considered to be toxic to humans by inhalation. Throughout the world, pollutant emission standards have become increasingly strict over the past ten years [3, 4]. The most effective wet processes use sodium or calcium hydroxides [5, 6, 7], but the liquid or solid wastes that absorption produced must be treated correctly if they are not marketable.

Ammonia-based wet flue gas desulphurization has drawn increasing attention because of its higher desulphurization efficiency, useful byproducts, and lower investment in china in recent years [8, 9].Liu Guorong [10] investigated the effects of several key factors on the efficiency of ammonia desulphurization and established a mathematical model for ammonia desulphurization based on the two-film theory in spray towers. Jia Yong [11] studied the gas-liquid mass transfer and chemical reaction process during ammonia-based flue gas desulfurization in a packed column. Gao Xiang [12] investigated the characteristics of the gas-liquid absorption reaction between sulfur dioxide and an ammonium sulfite solution in a stirred tank reactor and indicated that the absorption of sulfur dioxide is controlled by both the gas-and liquid-films when the ammonium sulfite concentration is lower than 0.05mol/L, and mainly by the gas-film at higher concentrations.

The aim of this study was to investigate the characteristics of SO_2 absorption into aqueous ammonia solutions and develop a model for the design and simulation of wetted-wall column used for absorption of SO_2 into aqueous ammonia.

EXPERIMENTAL SECTION

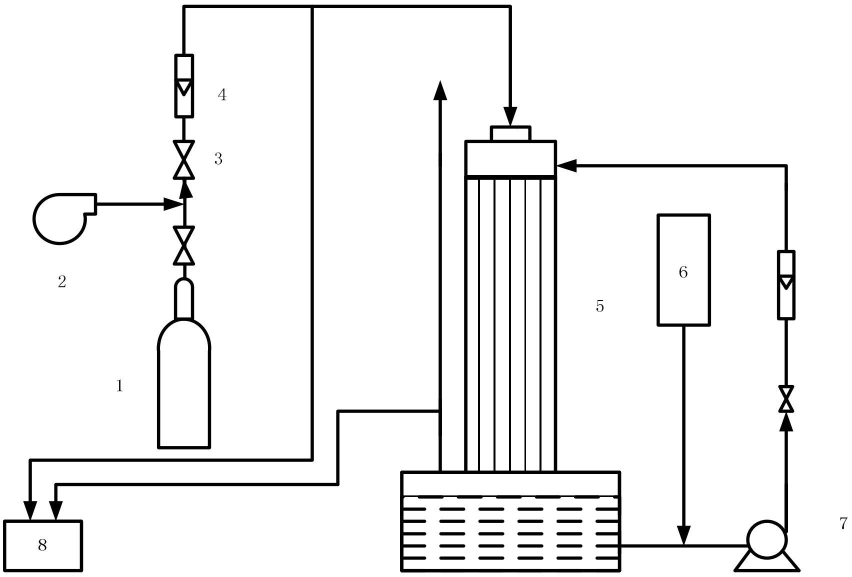
The experimental set-up is shown schematically in Fig. 1.It includes a pilot-scale column and a heat exchanger and a pump resistant to acid or alkali solutions. The tower has an inside diameter of 0.1m and is packed with ceramic tube which has an inside diameter of 8mm and outside diameter of 10mm. The number of ceramic tube is 38 and the height of the packing is 1.2m.

The gaseous mixture is made of SO_2 supplied by a high pressure cylinder and air blown by a compressor. Sample of gas at the input and the output of the column is analyzed by UV analyzer, which gives the SO_2 contents.

Efficiency of desulphurization is defined according to measured results for gas composition.

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \tag{1}$$

The column is operated co-currently with recycle of the scrubbing liquid, aqueous ammonia solution was used.
A series of absorption tests was conducted at 20±0.5□ and atmospheric pressure. Experiments were performed with gas flow rates in the range from $15m^3/h$ to $85m^3/h$ and a liquid flow rate varying between 0.05 m^3/h and 0.15 m^3/h.



1. SO_2 cylinder 2. Compressor 3.Valve 4. rotameter 5. Wetted-wall column 6. Ammonia liquor tank 7.Pumb 8.UV analyzer

Fig 1 Diagram of experimental system of ammonia desulphurization

MODELING OF SO_2 ABSORPTION INTO AQUEOUS AMMONIA SOLUTION

1Mass Transfer Characteristics of the Packing

The simulation of experimental results required the knowledge of the mass transfer characteristics of the absorption device for nominal liquid and gas flow rates.

A schematic representation of a fluid film flowing down on a vertical tube with gas phase is showed in Fig.2.
We make an overall mass balance of SO_2 or CO_2 over the slice of length *DH* shown in Fig.2

$$Q_G dC = 2N \ n(R-\delta)\pi dh \tag{2}$$

Where *n* is number of ceramic tube.

Where the mean film thickness *δ* is calculated from one of the following correlations,

$$\delta = \left(\frac{3\mu_L \Gamma}{\rho_L^2 g}\right) \quad \text{at } \mathrm{Re}_L < 20\sim40, \tag{3}$$

$$\delta = \left(\frac{2.4\mu_L \Gamma}{\rho_L^2 g} \right)^{1/3} \quad \text{at } 40 < \mathrm{Re}_L < 1200 \qquad (4)$$

Where

$$\mathrm{Re}_L = \frac{4\Gamma}{\mu_L} \qquad (5)$$

$$\Gamma = \frac{Q}{2n\pi R} \qquad (6)$$

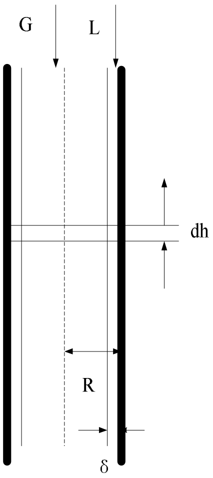


Fig 2 Schematic representation of film flowing down in a cylinder

The gas mass-transfer coefficient k_G was determined by absorbing SO_2 into sodium hydroxide solutions of concentrations 0.5 mol/L. In this system, the liquid-phase mass transfer resistance can be considered negligible [13]. A different mass balance over the gas phase for the absorbed component produces the following equation for calculation of k_G.

$$k_G = \frac{Q_G}{2n\pi(R-\delta)} \ln\left(\frac{C_{SO_{2,in}}}{C_{SO_{2,out}}}\right) \qquad (7)$$

The liquid-phase mass-transfer coefficient k_L was measured by absorbing 10% pure CO_2 into water. The gas-phase mass transfer resistance was assumed to be negligible because CO_2 has a low solubility in water.
The mean mass transfer coefficient k_L is calculated from [14]

$$k_{L,CO_2} = \frac{Q_L}{2n\pi(R-\delta)} \ln \frac{C_s - C_{L,in}}{C_s - C_{L,out}} \qquad (8)$$

For the experimental system, $k_{L,SO2}$ can be calculated by the correction formula as follows:

$$k_{L,SO_2} = k_{L,CO_2} (D_{SL} / D_{CL})^{2/3} \qquad (9)$$

Cs is calculated using Henry's law

$$C_s = \frac{p}{H} \qquad (10)$$

The partial pressure of the absorbed gas, *p*, is obtained from the gas-phase measurements. The solubility of CO_2 in water can be calculated by the following equation:

$$H_{CO_2} = 2.8249\times10^{6}\exp(\frac{-2044}{T}) \quad (11)$$

D_{SL}, D_{CL} can be calculated by the following equation [15]:

$$D_{AB(l)} = 1.173\times10^{-16}(\phi M_B)^{1/2}\frac{T}{\mu_B V_A^{0.6}} \quad (12)$$

Experimental parameters and dimensions are listed in Table 1 and the physical parameters in Table 2

Table 1Experimental parameters and dimensions

Liquid flow, Q_L	0.05-0.15m^3/h
Gas flow, Q_G, at 20□ and 1atm	15-85m^3/h
Temperature, T	20℃
Height of column, h	1.2 m
Pressure, P	1atm

Table 2 Physical parameters at 20℃

Water density, ρ_L	998kg/m^3
Dry air density, ρ_G	1.205 kg/m^3
Water viscosity, μ	1×10^{-3}Pa·s
Diffusion coefficient for CO_2 in water	1.78×10^{-9} m^2/s
Diffusion coefficient for SO_2 in water	1.52×10^{-9} m^2/s

The modified gas-phase mass transfer coefficient, $k_{G,}$ was investigated at different gas and liquid flow rates and calculated by eq (7).The gas-phase mass transfer coefficient at different gas and liquid flow rates have been plotted against empty section gas velocity and presented in Fig.3.It can be seen that as empty section gas velocity increases the gas-phase mass transfer coefficient increases, and so is the case with increase in liquid flow rates.

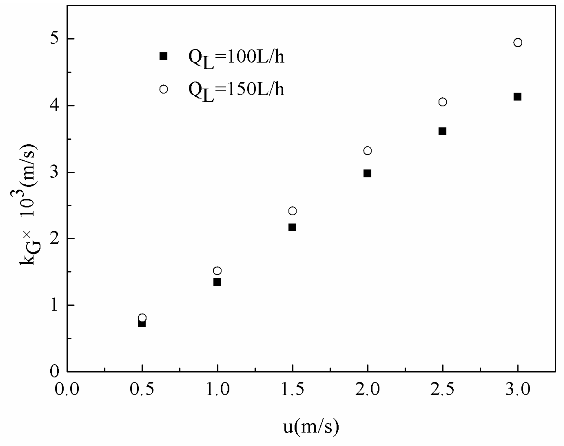


Fig 3 Effect of empty section gas velocity on k_G

The modified liquid-phase mass transfer coefficient, $k_{L,}$ was investigated at different gas and liquid flow rates and calculated by eq(8,9). The effect of liquid flow rate on Liquid-phase mass transfer coefficient is presented in Fig.4 at different gas flow rates. It can be seen from the figure that liquid-phase mass transfer coefficient increases as the liquid flow rate increases.

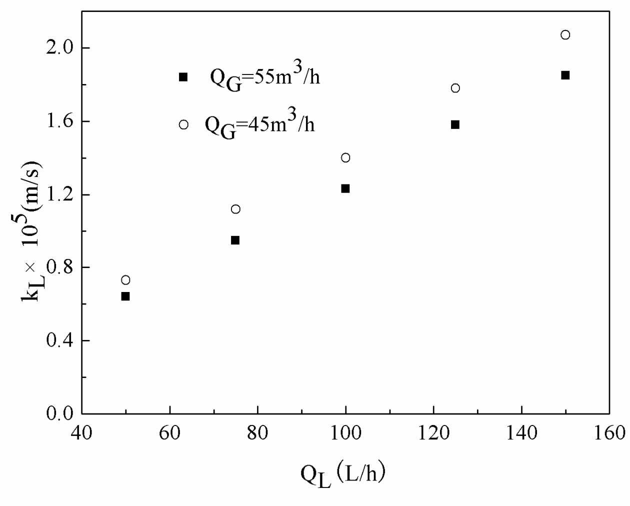


Fig 4 Effect of liquid velocity on k_L

The following assumptions were established to obtain a infinitesimal tower model with chemical reaction: reactions were completed within the film and can be instantaneous chemical equilibrium and charge balance; oxidation of sulfite was ignored; isothermal operation; the gas and liquid phases are in plug flow.

When dilute SO_2 is absorbed into aqueous ammonia solutions, the following reactions should be considered:

SO_2 (aq) +H_2O ƒ H_2SO_3 ƒ H^++HSO_3^- (13)
HSO_3^- ƒ H^++SO_3^{2-} (14)
HSO_3^-+1/2O_2 ƒ H^++SO_4^{2-} (15)
NH_3 (aq) +H_2O ƒ NH_4^++OH^- (16)
H_2O ƒ H^++OH^- (17)

2.1 Absorption model
According diffusion law[11]:

$$D(SO_2)\frac{d^2c(SO_2)}{dx^2}+D(HSO_3^-)\frac{d^2c(HSO_3^-)}{dx^2}+D(SO_3^{2-})\frac{d^2c(SO_3^{2-})}{dx^2}=0 \tag{18}$$

Boundary conditions at the interface(x=0)

$$N_{SO_2}^g=k_{G,SO_2}(p(SO_2)-p(SO_{2,i}))=-(D(SO_3^{2-})\frac{dc(SO_3^{2-})}{dx}|_{x=0}+D(HSO_3^-)\frac{dc(HSO_3^-)}{dx}|_{x=0}+ D(SO_3^{2-})\frac{dc(SO_3^{2-})}{dx}|_{x=0}) \tag{19}$$

$$D(H^+)\frac{dc(H^+)}{dx}|_{x=0}+D(NH_4^+)\frac{dc(NH_4^+)}{dx}|_{x=0}-D(OH^-)\frac{dc(OH^-)}{dx}|_{x=0}- D(HSO_3^{2-})\frac{dc(HSO_3^{2-})}{dx}|_{x=0}-2D(SO_3^{2-})\frac{dc(SO_3^{2-})}{dx}|_{x=0}=0 \tag{20}$$

Boundary conditions in bulk liquid(x=δ)

$$c(S-total)=c(SO_2)+c(HSO_3^-)+c(SO_3^{2-}) \tag{21}$$

$$c(N-total)=c(NH_4^+)+c(NH_3) \tag{22}$$

$$c(H^+)+c(NH_4^+)-c(OH^-)-c(HSO_3^-)-2c(SO_3^{2-})=0 \tag{23}$$

2.2 Reactor model
From fig.5 the steady-state mass balance of SO_2 in the gas phase plug flow through the column can be written as

$$(\frac{G}{RTS})\frac{\mathrm{d}p_{SO_2,b}}{\mathrm{d}z} = N^{g}_{SO_2,i}a \qquad (24)$$

Where N is flux of component A, kmol.m^{-2}.s^{-1}, p is partial pressure of component, kPa, G is gas volume flow rate,m^3 .s^{-1}. The steady- state mass balance for each species A($SO_{2(aq)}$、SO_3^{2-}、HSO_3^-、H^+、OH^-) in the bulk liquid phase is

$$\frac{L}{S}\frac{\mathrm{d}c_{A,b}}{\mathrm{d}z} = N^{l}_{A,b}a + R_{A,b}\varepsilon_l \qquad (25)$$

Where L is liquid volume flow rate,m^3 •s^{-1}, R_A is reaction rate of the component A, kmol•m^{-3}•s^{-1}.According to the law of elemental conservation, the steady- state fluxes of total S species through the liquid film are constant and are equal to SO_2 fluxes at the gas side.

Therefore, total S species in the liquid phase can be written as

$$\frac{L}{S}\frac{\mathrm{d}c_{S-total}}{\mathrm{d}z} = N^{g}_{SO_2,i}a \qquad (26)$$

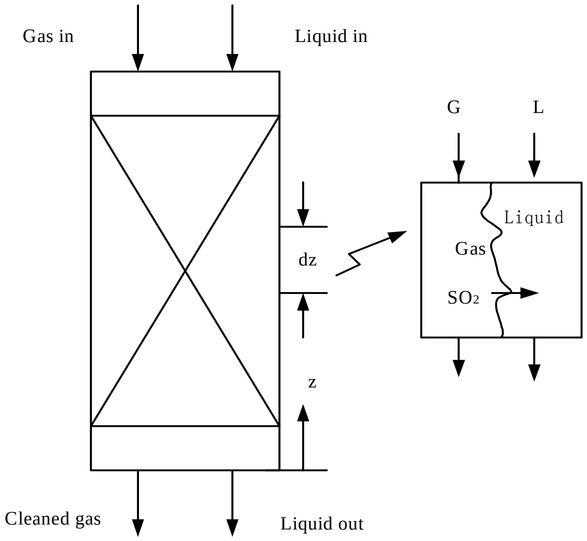


Fig.5 Diagram of material balance calculation of Absorber

2.3 Vapor-liquid equilibrium

In the liquid film, reactions(13)、(14)、(16)、(17)can reach equilibrium instantaneously and chemical equilibrium relations of these reactions in liquid can be achieved.

$$K_1 = \frac{c_{\mathrm{H}^+}c_{\mathrm{HSO}_3^-}}{c_{\mathrm{SO}_2}} \qquad (27)$$

$$K_2 = \frac{c_{\mathrm{H}^+}c_{\mathrm{SO}_3^{2-}}}{c_{\mathrm{HSO}_3^-}} \qquad (28)$$

$$K_3 = \frac{c_{\mathrm{OH}^-}c_{\mathrm{NH}_4^+}}{c_{\mathrm{NH}_3}} \qquad (29)$$

$$K_W = c_{\mathrm{H}^+}c_{\mathrm{OH}^-} \qquad (30)$$

Where K is equilibrium dissociation constants

3 Solving model

In the model the diffusion coefficients of gases were calculated from Fuller empirical formula and the diffusion coefficients in liquid use the data of literature of 13.extrapolated diffusion constants from 25℃ to 55℃ using the Stokes-Einstein equation [14].the dissociation equilibrium constants and solubility values for SO_2 and NH_3 were estimated by correlation of literature15.the thickness of film was estimates by formula of literature16, 17.

In summary, the model includes the mass balance equations, the interface equilibrium equations, electrically neutral equations, chemical equilibrium equations, integral equations of mixture. The above equation can be obtained simultaneous concentration distribution of SO_2、HSO_3^-、SO_3^{2-}、H^+、OH^- component in a certain section in the film. And then the components of the flux and parameters change along the tower height were get after integral mass balance equations of vapor and liquid phase main tower

4 Model parameters

The inlet SO_2 concentration is 2500mg •m^{-3}, the absorption efficiency is 92%, with 4% aqueous ammonia solution to adjust the pH of the absorption liquid.

The parameters used in the simulation are shown in Table3.

Table.3 model parameters for the SO_2 absorption into ammonia solutions

T(K)	298	$D(SO_3^{2-})(m^2/s)$	0.943×10^{-9}
p(kPa)	101.325	$D(SO_2)(m^2/s)$	1.799×10^{-9}
$G(m^3 \cdot h^{-1})$	50	$D(NH_3)(m^2/s)$	1.612×10^{-9}
$L(L \cdot h^{-1})$	120	$k_L(m \cdot s^{-1})$	1.58×10^{-5}
pH	6.5	$H(kPa \cdot m^3 \cdot kmol^{-1})$	80.686
$k_G(kmol \cdot m^{-2} \cdot s^{-1} \cdot kPa^{-1})$	3.1×10^{-3}	K_1	0.0136
$D(H^+)(m^2/s)$	9.155×10^{-9}	K_2	6.69×10^{-8}
$D(OH^-)(m^2/s)$	5.185×10^{-9}	K_W	6.95×10^{-15}
$D(NH_4^+)(m^2/s)$	1.93×10^{-9}	c_{NH4^+} $(kmol \cdot m^{-3})$	0.6
$D(HSO_3^-)(m^2/s)$	1.519×10^{-9}		

RESULTS AND DISCUSSION

1 Concentration profiles in the liquid film

P_H and concentration distribution of each component in the liquid film at the top of the column were calculated by the model which shown in Fig. 6. Abscissa x is the ratio of the distance of a different location from the gas-liquid interface and the film thickness δ. The concentration of NH_4^+ evenly distributed through the film. From the results of Fig. 6 may determine a hypothetical reaction interface, the film is divided into two areas. The first region adjacent the interface, the concentration of SO_2 is significant, occurs rapidly reversible hydrolysis, and the second region near the bulk liquid where the concentration of SO_2 is negligible.

2 Enhancement factor along the column

Enhancement factor can be defined as the ratio of actual rate of absorption and the absorption rate with the same driving force without chemical reaction [18].

$$E = \frac{N_{SO_2}}{k_{l,SO_2}\left(c_{SO_2,(aq)}|_{x=0} - c_{SO_2,(aq)}|_{x=\delta}\right)} \tag{31}$$

Enhancement factor can be estimated using the model at the determined chemical composition of gas and liquid.

Results shown in Fig.7. The enhancement factor reaches its maximum at the top of tower and gradually reduced with the pH value decreased from the top of the tower to the bottom of the tower. The figure shows enhancement factor is still greater even near the bottom of the column. Mass transfer resistance is mainly concentrated in the gas phase and the absorption process is gas film resistance control process.

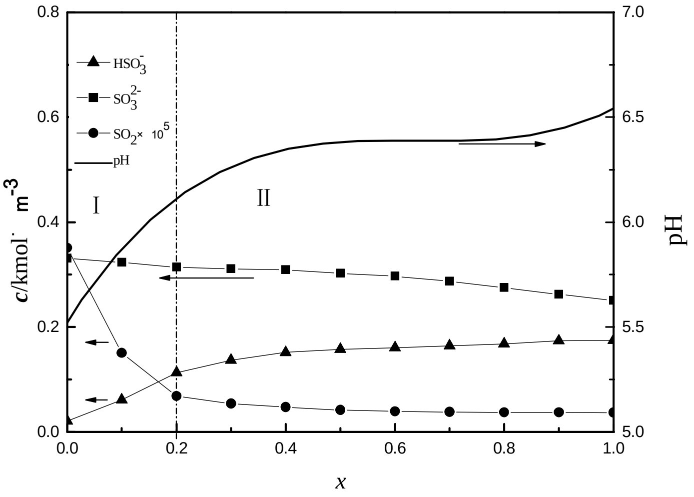


Fig.6 Concentration profiles calculated in the liquid film (*z*=*h*)

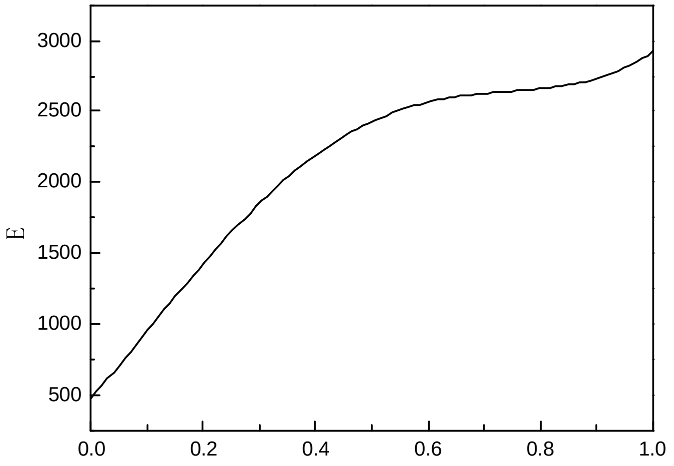


Fig.7 Chemical enhancement factor for SO_2 absorption along the column

3 Effect of the SO2 inlet concentration on desulphurization efficiency

When pH of the absorbent solution is 6.5±0.1, flue gas flow is 50m^3/h, concentration of SO_2 change from 1000mg/m^3 to 3000 mg/m^3, the desulfurization rate variation shown in Fig.8. Prediction results are agreement with the experimental data.

CONCLUSION

The kinetic parameters relative to SO_2 absorption into aqueous solutions of ammonia previously determined from laboratory measurements.Mathematical model of absorption SO_2 with ammonia solution in wetted tower basis of two-film theory can be used to describe this complex multicomponent absorption process. The model can calculate the concentration of each component distribution curve of liquid film and enhancement factor changes along the column. Based on simulation results verify the impact of imports of SO_2 concentration on the absorption rate, the results show that the model predictions are consistent with experimental results.This model, coupled with the determination or the estimation of mass-transfer characteristics can be applied to the simulation or design of industrial scrubbers.

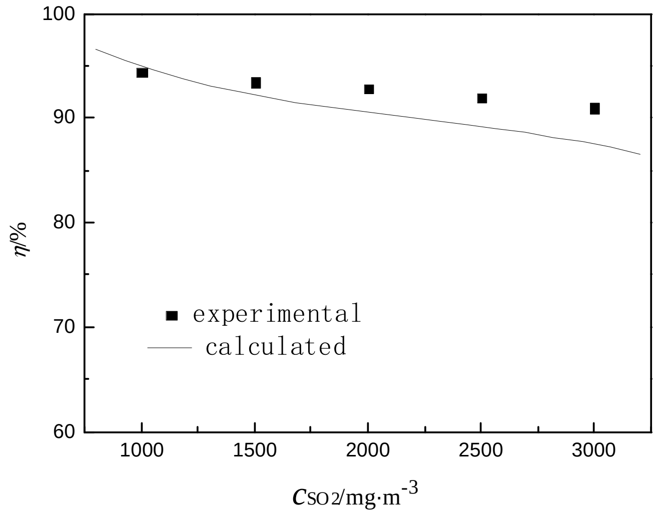


Fig.8 Effect of the SO_2 inlet concentration on desulphurization efficiency

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