A Simple Mathematical Model and Computer Simulation of Non-isothermal Gas Absorption in Packed Tower

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Abstract. Oxygen-enriched combustion technology can effectively achieve residual capture, but the existence of acid gases such as NO$_x$ and SO$_x$ is not conducive to the transportation and storage of CO$_2$. The compression of CO$_2$ discharged from the packed tower is a necessary process before transportation. Therefore, the study of combined desulfurization and denitrification of flue gas under high pressure is of great significance to the application of carbon capture and storage technology. Based on the mass transfer coefficients obtained from experiments, a coupled model of mass transfer and kinetics of the bubbling reactor is established for the combination of reaction mechanism and kinetics of non-isothermal gases, and this unsteady state problem is solved by the Runge-Kutta mathematical method. The simulation study of the product changes in the process of NO and SO$_2$ absorption alone and combined absorption under different pressures. The results show that: the interaction of NO$_x$ and SO$_x$ in the liquid phase promotes the absorption of SO$_2$, NO and the mass production of SO$_4^{2-}$ and HSO$_4^-$ in the liquid phase, and it also generates a large amount of greenhouse gas N$_2$O; the increase in pressure is beneficial to SO$_4^{2-}$, SO$_3^{2-}$, the production of HADS and HAMS also led to an increase in the production of N$_2$O.

Keywords: Oxy-fuel Combustion, Pressurization, Flue Gas, Desulfurization and Denitrification

1. Introduction
CO$_2$ emissions from packed towers are one of the main causes of the greenhouse effect. In recent years, oxyfuel combustion technology, also known as air separation/flue gas recirculation combustion technology, is considered to be one of the most promising technologies for direct emission reduction of coal-fired CO$_2$.$^{[1-3]}$. Pulverized coal oxy-fuel combustion technology can effectively reduce the NO$_x$ and SO$_x$ emissions per unit mass of fuel, and it make the CO$_2$ concentration in the flue gas reach more than 90%, but the NO$_x$ and SO$_x$ concentration in the flue gas are higher, even higher than that of air Combustion emission value. If the impurity gas in the flue gas is not removed, it will have an adverse effect on the subsequent transportation and storage of CO$_2$ or resource utilization. Therefore, the purification of oxy-fuel combustion flue gas is very important.$^{[4]}$

In the CO$_2$ compression process, high pressure and low temperature conditions can promote the conversion of NO$_x$ and SO$_x$ in the flue gas into nitric acid and sulfuric acid, so that the CO$_2$ gas can be
purified\textsuperscript{[5-6]}. To solve the problem of simultaneous desulfurization and denitrification in the CO\textsubscript{2} compression process, domestic and foreign researchers have carried out a large number of experimental studies, such as experimental studies on the desulfurization and denitrification process. The results show that the conversion rate of NO increases with the increase of pressure. When it reaches 2MPa or more, more than 90\% of NO will be converted into dilute nitric acid. The higher the initial NO concentration in the flue gas, the greater the conversion rate of NO, and the integrated removal of SO\textsubscript{2} and NO experimental research found that only a small amount of NO conversion For dilute nitric acid, SO\textsubscript{2} reacts first, and NO plays a catalytic role; research by foreign scholars has shown that increasing pressure, lowering temperature and proper residence time will promote the conversion of NO and SO\textsubscript{2} into nitric acid and sulfuric acid, respectively. There are relatively few simulation studies on simultaneous desulfurization and denitrification processes under high pressure. Simulation studies have found that the combined absorption process of SO\textsubscript{2} and NO mainly produces sulfuric acid and nitric acid; pH has a decisive effect on the entire absorption process; and a large amount of N\textsubscript{2}O is also produced. Existing simulation studies mainly focus on the dynamic changes of HNO\textsubscript{3}, HNO\textsubscript{2}, H\textsubscript{2}SO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}, but it lack the dynamic process of SO\textsubscript{2} and NO absorption into water under high pressure, the influence of the interaction of NO\textsubscript{x} and SO\textsubscript{x} on the absorption efficiency of SO\textsubscript{2} and NO, and it Research on the influence of pressure on the interaction of NO\textsubscript{x} and SO\textsubscript{x}.

In this paper, by establishing a mathematical model of mass transfer coupled chemical reaction, the non-isothermal gas absorption in the packed tower is studied, the interaction mechanism of NO\textsubscript{x} and SO\textsubscript{x} is revealed, and the effect of the mechanism on the absorption process is discussed, and which is a high-pressure combined desulfurization and denitration for oxy-fuel combustion. Provide reference for the application of technology.

2. Reactor model
In this paper, the previous difference method and Runge-Kutta iterative method are used to solve the one-dimensional unsteady-state equations. In order to ensure the calculation accuracy and make the reaction model close to the actual process, the calculation time step is set to 10\textsuperscript{-5}s, and it the entire reactor Discrete into N completely mixed batch reactors. The SO\textsubscript{2} mass transfer coefficient, bubble diameter, gas-liquid volume and gas-liquid contact surface area of reaction zone 2 corresponding to different pressures. The simulated flue gas enters from the inlet of the high-pressure bubbling reactor, passes through the reaction zones 1, 2 and 3 in turn, and it is finally discharged from the outlet. The high-pressure bubbling reactor model consists of 3 reaction zones: Reaction zone 1 is a gas-phase reaction zone (without steam); Reaction zone 2 is a gas-liquid reaction zone (with water vapor); Reaction zone 3 is a gas-phase reaction zone (with steam) water vapor). The gas phase of reaction zone 2 is assumed to be a plug flow reaction zone, where the gas phase zone is divided into N equal gas phase zones (the number of grids), and the liquid phase is a complete premixed reaction zone. The basic equation of the gas phase zone is equation (1), and the basic equation of the liquid zone zone is equation (2).

\[
\frac{dC_{a,i}}{dt} = \frac{-G}{V_{G}} \left( C_{a,i} - C_{a,i-1} \right) + 1000 \times J_{a,i} \times a + R_{k,a,i} \tag{1}
\]

\[
\frac{dC_{b,i}}{dt} = \sum R_{k,b} - \sum_{i=1}^{N} 1000 \times J_{b,i} \times a \tag{2}
\]

Where: C is the concentration, mol/L; t is the time, s; G is the volume flow, m\textsuperscript{3}/s; V_{G} is the volume of the gas phase zone, m\textsuperscript{3}; a is the specific surface area, m\textsuperscript{-1}; J is the mass transfer flux, mol/(m\textsuperscript{2} \times s); Rk is the chemical reaction rate, mol/(L \times s); A is the gas phase composition; B is the liquid phase composition; N is the number of grids in the gas phase reaction zone; g is the gas phase; l is Liquid phase.
3. Chemical reaction
In the gas phase reaction zone, NO is first oxidized by O\textsubscript{2} to produce NO\textsubscript{2} (R1), and its rate increases significantly with pressure increase and temperature decrease. In the gas phase reaction zone, NO and NO\textsubscript{2} further react with H\textsubscript{2}O to form HNO\textsubscript{2} (R2); in the liquid phase reaction zone, NO\textsubscript{2} dissolved in water will react with H\textsubscript{2}O to form HNO\textsubscript{2} and HNO\textsubscript{3} (R3), and the unstable HNO\textsubscript{2} will be further decomposed into HNO\textsubscript{3} and NO (R4).

SO\textsubscript{2} and H\textsubscript{2}O undergo a hydrolysis reaction to generate HSO\textsubscript{3}\textsuperscript{−} (R5), and a part of HSO\textsubscript{3}\textsuperscript{−} will be further ionized to SO\textsubscript{3}\textsuperscript{2−} (R6). HSO\textsubscript{3}\textsuperscript{−} and SO\textsubscript{3}\textsuperscript{2−} may be oxidized by O\textsubscript{2} and NO\textsubscript{2} dissolved in water to form stable H\textsubscript{2}SO\textsubscript{4} (R9-R10). In the liquid phase, HSO\textsubscript{4}\textsuperscript{−} will be partially ionized into SO\textsubscript{3}\textsuperscript{2−} (R11). In the liquid phase reaction zone, H\textsubscript{2}SO\textsubscript{3} will also form important intermediate nitrogen and sulfur products with HNO\textsubscript{2}, such as NSS(NOSO\textsubscript{3}−), HADS(HNO(SO\textsubscript{3}2−)), and HAMS(HNOHSO\textsubscript{3}−). NSS is formed by reaction (R12), and NSS is further hydrolyzed to generate H\textsubscript{2}SO\textsubscript{4} and HNO (R13), and HNO will further react to generate stable greenhouse gas N\textsubscript{2}O (R15). The formation of RADS is due to the reaction (R14) and its hydrolysis reaction products are HAMS and H\textsubscript{2}SO\textsubscript{4} (R16).

4. Simulation results

4.1. SO\textsubscript{2} absorption simulation
Figure 1 is a comparison of simulation and experimental results of the change of SO\textsubscript{2} concentration in the outlet gas phase after absorption by different numbers of completely mixed batch reactors. It can be seen that when N=5, the difference between the simulation and the experimental results is relatively large, as N increases, the simulation results are closer to the experimental results, and which shows that the accuracy of the simulation results has a great relationship with N. When N>25, and the effect of N on the absorption of SO\textsubscript{2} by water is not obvious, which means that when N reaches a certain amount, and it can be ensured that the reaction model used in the simulation process is close to the actual reactor.

Figure 2 shows the comparison of the simulation and experimental results of the concentration changes of SO\textsubscript{2} absorbed into the water with different concentrations. The simulation results are in good agreement with the experimental results, especially when the SO\textsubscript{2} concentration is 1500cm\textsuperscript{3}/m\textsuperscript{3}, the simulation results are basically consistent with the experimental results. It can be seen from Figure 2 that the SO\textsubscript{2} concentration in the outlet gas phase increases with the increase of the SO\textsubscript{2} inlet concentration and the absorption time. This is because the solubility of SO\textsubscript{2} in water is limited. As the dissolved SO\textsubscript{2} in water approaches its saturated solubility, the water absorbs The rate of SO\textsubscript{2} is getting smaller and smaller.

![Figure 1](image-url)
Through the balance calculation of import and export nitrogen (or sulfur) elements, the accuracy of the simulation itself can be verified. The accuracy of the calculation result is defined as: the ratio of the amount of nitrogen (or sulfur) related components of the gas inlet to the sum of the gas outlet and the location of the nitrogen (or sulfur) related components remaining in the reactor. Through calculation, the accuracy of sulfur and nitrogen elements under different pressures are both > 99.0%. Therefore, the calculation result is reliable.

From the change of the liquid phase products absorbed by $SO_2$ into the water, it can be seen that $S(IV)$ in the liquid phase mainly exists in the form of $3HSO_3^-$, while $SO_3^{2-}$ and $SO_4^{2-}$ are basically absent. Other research results show that $SO_3^{2-}$ is also the main product and accounts for about 30% of total sulfur. This may be due to the fact that $HSO_3^-$ in the solution was oxidized to $H_2SO_4$ during the storage and detection process of the absorption solution after the experiment.

There is an equilibrium between $HSO_3^-$ and $SO_2$ in the solution. In the initial stage, the concentration of $HSO_3^-$ in the solution is 0, so $SO_2$ is rapidly absorbed in the initial stage; as the value of $SO_2$ absorbed by water gradually increases, the concentration of $HSO_3^-$ and $H^+$ in the solution increases continuously, resulting in the reaction rate of reaction (R5) decline.

4.2. NO absorption simulation

From the simulation results of the changes in the vapor and liquid phase products absorbed by NO into the water, it can be seen that when the pressure is 1.5 MPa, NO can be oxidized to NO$_2$ that is easily soluble in water, as time goes by, the NO$_2$ concentration in the outlet gas phase gradually increases. This is because NO, the product of decomposition of HNO$_2$ accumulated in the solution, is released into the gas phase and quickly oxidized to NO$_2$, resulting in an increase in the NO$_2$ concentration in the outlet gas phase. It can be seen from the results that the concentration of NO$_2^-$ in the solution rises rapidly at the initial stage and then decreases, while the concentrations of HNO$_2$ and NO$_3^-$ continue to increase. There is a balance between HNO$_2$ in the solution and its ionized products ($H^+$ and NO$_3^-$.). As the reaction progresses, the $H^+$ concentration increases, resulting in a decrease in the ionization rate of HNO$_2$, and which makes the concentration of HNO$_2$ in the solution increase and the concentration of NO$_3^-$ decreases. The increasing concentration of NO$_3^-$ in the solution comes from the decomposition of HNO$_2$ to produce HNO$_3$, and the reaction of NO$_2$ with H$_2$O to produce HNO$_3$, which then ionizes to NO$_3^-$. 

4.3. Simulation of joint absorption of $SO_2$ and NO under different pressures
The simulation results of the changes in the gas and liquid phase products of \( \text{SO}_2 \) and \( \text{NO} \) jointly absorbed into water under different pressures. From Figures 1a and 1b, it can be seen that the higher the pressure, the more favorable the reaction (R1) and the absorption of \( \text{NO}_2 \) and \( \text{SO}_2 \) by water, but it also leads to an increase in the amount of \( \text{N}_2\text{O} \) produced. It can be seen that pressure has a greater impact on the production of \( \text{HSO}_3^- \), but it has little effect on the production of \( \text{SO}_3^{2-} \), that is, when the pressure is 0.5MPa, the production of \( \text{HSO}_3^- \) is the most; when the pressure is 1.5MPa, and the production of \( \text{HSO}_3^- \) is the least. This shows that the higher the pressure, the better the conversion of \( \text{HSO}_3^- \) into \( \text{H}_2\text{SO}_4 \) and other intermediate nitrogen and sulfur products. It can be seen that the increase in pressure is beneficial to the generation of \( \text{SO}_3^{2-} \) and \( \text{NO}_3^- \). It can be seen that N-S complex compounds are mainly HADS and HAMS. With the increase of pressure, the production of HADS and HAMS slightly increases, indicating that the increase of pressure promotes the reaction (R14) and (R16).

### 5. Conclusion

The compression of \( \text{CO}_2 \) produced by the packed tower is a necessary process before transportation. Therefore, the study of combined desulfurization and denitrification of flue gas under high pressure is of great significance to the application of carbon capture and storage technology. The simulation results of the absorption of \( \text{SO}_2 \) and \( \text{NO} \) separately show that the liquid phase products containing sulfur are mainly \( \text{HSO}_3^- \); the liquid phase products containing nitrogen are mainly \( \text{HNO}_3 \) and \( \text{NO}_3^- \). The simulation results of the combined absorption of \( \text{SO}_2 \) and \( \text{NO} \) under different pressures show that the higher the pressure, the more favorable the production of \( \text{SO}_3^{2-} \), \( \text{NO}_3^- \), HADS and HAMS, and \( \text{N}_2\text{O} \).

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