

Experimental and Theoretical Studies on Desulfurization Efficiency of Dual-alkali FGD System in a RST Scrubber

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Abstract: The effects of operating parameters on desulfurization efficiency of a dual-alkali FGD process in a rotating-stream-tray (RST) scrubber are investigated. A dimensionless factor, ε , is proposed in this study to predict desulfurization efficiency of this dual-alkali FGD system. ε represents the desulfurization ability of a dual alkali FGD system, determined by five main operating parameters such as sodium ion concentration, ratio of absorbent flow rate to flue gas flow rate, pH value of absorbent solution, ratio of sulfate ion to total sulfur ion in absorbent solution, and sulfur dioxide concentration of inlet flue gas. The empirical expression for predicting desulfurization efficiency at different temperatures is obtained through the experimental study and theoretical calculation. It provides useful guide for engineering design.

Key words: desulfurization; efficiency; dimensionless factor; dual-alkali FGD; RST scrubber

CLC No: X701.3 **Document Code:** A **Article ID:** 1009-606X(2006)05-0718-06

1 INTRODUCTION

In the field of flue gas desulfurization (FGD) technologies, lime/limestone-gypsum FGD is the dominant technology, but scaling and plugging are big obstacles^[1]. Dual-alkali FGD process was proposed and widely used^[2,3] in industry to reduce the effects of scaling and plugging of the lime/limestone-gypsum FGD process. Wang et al.^[4] described a sodium-limestone dual-alkali flue gas desulfurization process, in which the effluent absorbent solution consisted of aqueous sodium sulfite and sodium bisulfite solution with pH=5.8~6.6 and sodium concentration of 0.5~0.9 mol/L and it was regenerated with sufficient ground limestone. After regeneration, the solution had a pH value between 6.3 and 7.0, and the bisulfite concentration was reduced by 35%~70%. The desulfurization efficiency was about 90%. Similar dual-alkali processes for sulfur dioxide removal were proposed in the literature^[5,6]. Yu^[7] studied the effects of main operating parameters on desulfurization efficiency of sodium-calcium dual alkali FGD process in a laboratory-scale scrubber with fiber railing panels. Li et al.^[8], Wu et al.^[9] and Yan et al.^[10] experimentally studied the Na₂CO₃-Ca(OH)₂ dual-alkali FGD processes in a rotating-stream-tray (RST) scrubber. The

main parameters (such as liquid/gas ratio, Na⁺ and SO₄²⁻ concentrations in the solution, pH of absorbent solution and SO₂ concentration of inlet flue gas) affecting SO₂ removal efficiency were investigated. It was concluded that the desulfurization efficiency of about 80% could be obtained when [Na⁺] reached 0.3 mol/L.

However, the effect of temperature on the desulfurization was not discussed in these studies^[7-10]. And there were few on the theoretical study of the desulfurization efficiency. Based on the work of literature, the experimental and theoretical studies of Na₂CO₃-Ca(OH)₂ dual-alkali process in a RST scrubber are carried out in this work. And the effect of flue gas temperature is also investigated.

2 EXPERIMENTAL

In order to obtain the relationship between desulfurization efficiency (η) and the five operating parameters, experimental work is carried out in a laboratory-scale setup (Fig.1). The absorbent liquid consists of sodium carbonate at different initial concentrations, when sulfur dioxide is absorbed into the solution, sodium sulfite and sodium bisulfite are produced. The ratio of sulfite to bisulfite is determined by pH value. Experimental conditions are listed in Table 1.

Received date: 2005-08-09; **Accepted date:** 2005-12-06

Foundation item: Supported by the National Hi-tech Research and Development Program (863 program) of China (No.2001AA642030-1); Key Research Project of Zhejiang Province (No.2004C23028); New Century Excellent Scholar Program of Ministry of Education of the People's Republic of China (No.NCET-04-0549)

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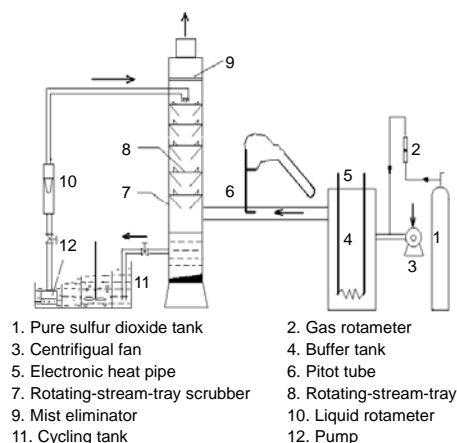


Fig.1 The experimental setup of dual-alkali FGD

Table 1 Experimental conditions

Diameter of RST scrubber	150 mm
Number of RST	5
Tray spacing (mm)	200
[Na ⁺] (mol/L)	0.1~1.0
Gas flow rate, G (m ³ /h)	160
Liquid flow rate, L (L/h)	160~800
pH	5.00~9.00
Sulfur dioxide concentration, C_{SO_2} (mg/m ³)	400~5 000
Ratio of sulfate ion to total sulfur, x	0~0.95
Gas temperature (°C)	30, 60, 90, 120

The sodium ion concentration is measured by ion chromatogram (Dionex DX-80). The concentration of the total oxidizable sulfur (TOS) is determined by iodometric titration, and the concentration of sulfate ion is measured by barium sulfate precipitation titration. The sulfur dioxide concentration in the inlet flue gas is measured by a flue gas analyzer (Kane–May KM9106). pH value is measured by a pH meter, Mettler Toledo Delta 320. And the flue gas and absorbent flow rates are measured by a pitot tube and a rotameter, respectively.

2.1 Setup and Procedure

The experimental setup is shown in Fig.1. Simulated flue gas is prepared in the buffer where pure sulfur dioxide and air from a centrifugal fan are mixed and heated. Then the simulated flue gas enters the bottom of the RST scrubber and becomes highly swirling bypassing through RST. Absorbent liquid is pumped to the top of the scrubber. The liquid is atomized by the rotating flue gas and absorbs the sulfur dioxide in the simulated flue gas simultaneously. Clean gas flows up through a mist eliminator and is vented into the environment. The absorbent after absorption flows back into the cycling tank for regeneration with lime slurry and clarified, and then recirculated to the scrubber. The amount of lime slurry added to the regeneration tank should maintain the absorbent pH value.

Detailed structure of RST is shown in Fig.2. The RST consists of blind ban, vane and downstream duct. The absorbent liquid flows onto the blind ban and radially to the scrubber wall. When the liquid flows over the vanes, it is atomized by the swirling gas. The droplets go to the wall by the centrifugal force and the liquid flows into the downstream duct^[11].

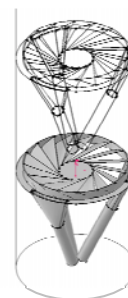


Fig.2 RST structure

2.2 Experimental Results

Figures 3~7 show the effects of sodium ion concentration, ratio of liquid flow rate to flue gas flow rate (L/G), ratio of sulfate ion to total sulfur, sulfur dioxide concentration and gas temperature on desulfurization efficiency. The efficiency is defined as

$$\eta = (1 - C_{SO_2, out} / C_{SO_2, in}) \times 100\% . \quad (1)$$

Figure 3 indicates that at a certain sodium ion concentration, the desulfurization efficiency increases asymptotically with the increase in pH. Further increase of pH contributes no evident increase to the efficiency when pH is in the range from 7.00 to 9.00. It is also known from Fig.3 that the relationship between the desulfurization efficiency and sodium ion concentration is similar to that between the desulfurization efficiency and pH. The optimum sodium ion concentration is about 0.3~0.5 mol/L, since high sodium concentration will lead to high sodium consumption due to solution loss in the calcium sulfite as solid waste.

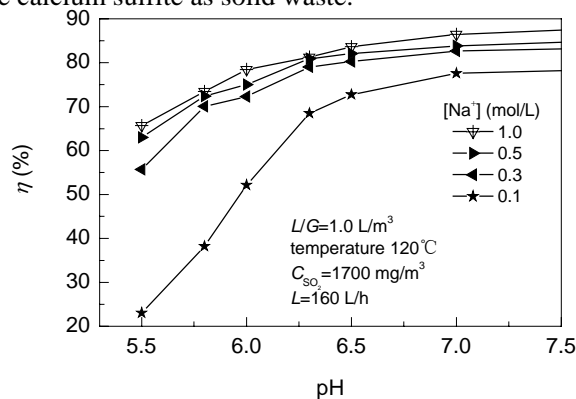


Fig.3 Effect of sodium ion concentration

It can be seen in Fig.4 that desulfurization efficiency increases with the increase in L/G value for more absorbent and more contact area in the scrubber. However, for a very high L/G value the cost of desulfurization and the total pressure drop will increase. The optimum value of L/G is about $1.0\sim 3.0\text{ L/m}^3$.

The effect of sulfate ion on desulfurization efficiency is shown in Fig.5. The desulfurization efficiency decreases with the increase in sulfate ion concentration at a certain sodium ion concentration. Increased sulfate ion concentration will reduce the sulfite ion concentration, so that the active sodium ion concentration decreases. Due to the excessive oxygen in the flue gas (about $5\%\sim 10\%$), sulfite oxidation is inevitable, which will do harm the desulfurization efficiency. Therefore, inhibiting sulfite oxidation in dual-alkali FGD process is necessary to improve the desulfurization efficiency.

Figure 6 shows that the desulfurization efficiency decreases with the rise of sulfur dioxide concentration in the inlet flue gas. Increasing the sulfur dioxide content will increase the amount of sulfur dioxide in absorbent

liquid. Hence, the gas phase sulfur dioxide equilibrium concentration increases as well.

The effect of gas temperature on desulfurization efficiency was seldom studied by former researchers^[7-10]. A high inlet gas temperature will slightly reduce the desulfurization efficiency (shown in Fig.7). Increasing gas temperature has two different effects on desulfurization. One effect is that when the gas temperature increases to $30, 60, 90$ and $120\text{ }^\circ\text{C}$, the temperature of absorbent solution also increases to $27, 39, 44$ and $48\text{ }^\circ\text{C}$, which will promote desulfurization efficiency due to higher absorption reaction rate. However, increasing temperature will decrease the solubility of sulfur dioxide, which results in the reduction of the mass transfer rate and the desulfurization efficiency. Because the absorption reaction between sulfur dioxide and sodium sulfite-bisulfite in solution is a quick reaction, the reaction rate is controlled by the mass transfer rate of sulfur dioxide from gas phase to liquid phase. The latter effect is dominant, and the desulfurization efficiency decreases with the increase in gas temperature.

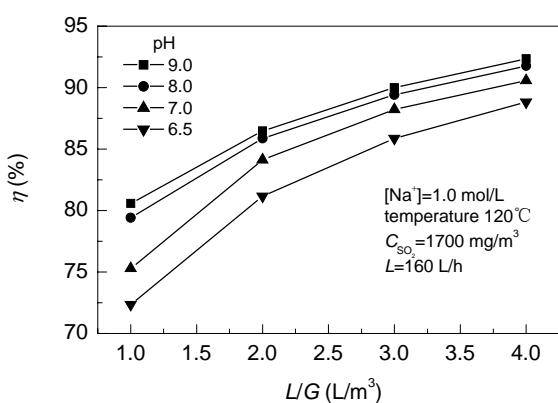
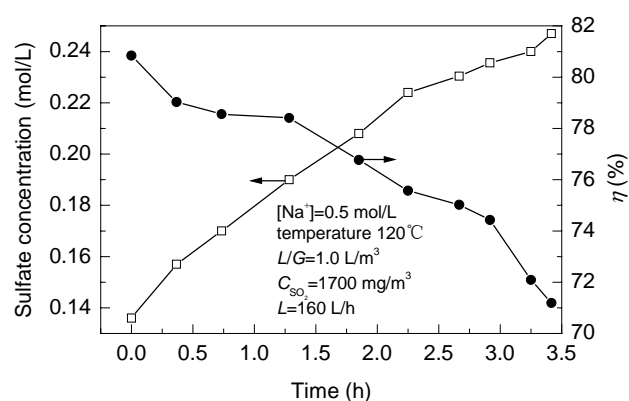
Fig.4 Effect of L/G 

Fig.5 Effect of sulfate ion concentration

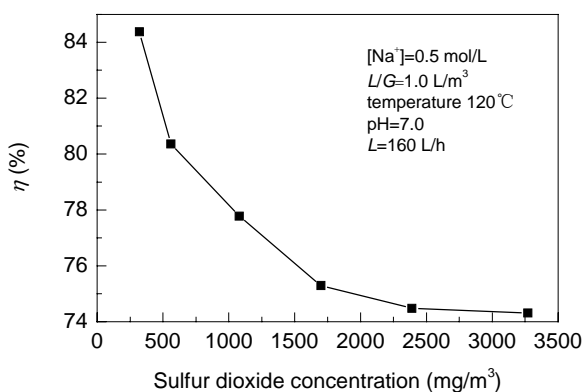


Fig.6 Effect of sulfur dioxide concentration

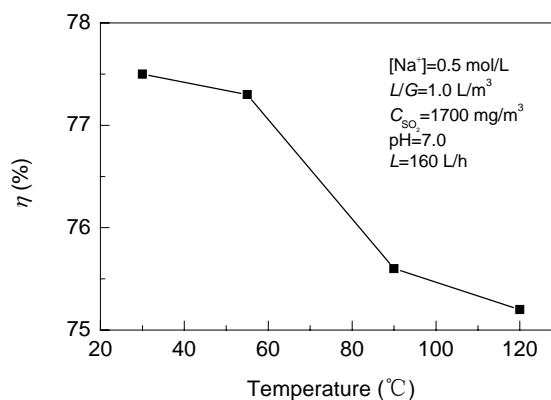


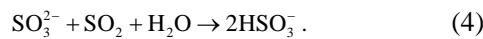
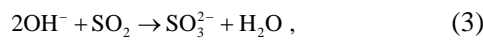
Fig.7 Effect of gas temperature

3 THEORETICAL STUDY

There are several ions in the absorbent liquid, such as sodium ion, hydrogen ion, calcium ion, sulfite ion, bisulfite ion, sulfate ion and hydroxide ion, etc. It is known that the absorbent is neutral, so the concentrations of the ions should satisfy the following equation:

$$[\text{Na}^+] + [\text{H}^+] + 2[\text{Ca}^{2+}] = [\text{OH}^-] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] + 2[\text{SO}_4^{2-}]. \quad (2)$$

The sulfite ion and hydroxide ion among these ions have the ability of absorbing sulfur dioxide. The absorption reactions can be written as



From Eqs.(3) and (4), the stoichiometric ratios of hydroxide to sulfur dioxide and sulfite to sulfur dioxide are 1:1. Therefore, the capacity of desulfurization (CS) is defined as the total concentration of sulfite and hydroxide ions as

$$\text{CS} = [\text{SO}_3^{2-}] + [\text{OH}^-]. \quad (5)$$

TOS is defined as

$$\text{TOS} = [\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]. \quad (6)$$

Total sulfur (TS) is

$$\text{TS} = [\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] + [\text{SO}_4^{2-}]. \quad (7)$$

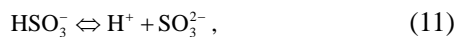
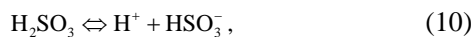
The ratio of sulfate ion to total sulfur, x , is given by

$$x = \frac{[\text{SO}_4^{2-}]}{\text{TS}}. \quad (8)$$

Thus, Eq.(8) can be rewritten as

$$[\text{SO}_4^{2-}] = \frac{x}{1-x} \text{TOS}. \quad (9)$$

There are several equilibria in the absorbent solution



The values of the three related equilibrium constants for Eqs.(10)~(12) are designated as K_{a1} , K_{a2} ^[12] and K_w ^[13] respectively. The constants K_{a1} and K_{a2} can be calculated by using Van't Hoff equation as follows:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H}{RT^2}, \quad (13)$$

where ΔH is the enthalpy change. From Eqs.(6), (10) and (11), the following equations can be derived:

$$[\text{H}_2\text{SO}_3]/\text{TOS} = [\text{H}^+]^2 / ([\text{H}^+]^2 + K_{a1}K_{a2} + K_{a1}[\text{H}^+]), \quad (14)$$

$$[\text{HSO}_3^-]/\text{TOS} = K_{a1}[\text{H}^+] / ([\text{H}^+]^2 + K_{a1}K_{a2} + K_{a1}[\text{H}^+]), \quad (15)$$

$$[\text{SO}_3^{2-}]/\text{TOS} = K_{a1}K_{a2} / ([\text{H}^+]^2 + K_{a1}K_{a2} + K_{a1}[\text{H}^+]). \quad (16)$$

Calculation result from Eq.(13) indicates that when pH is higher than 5.0, the sulfurous acid concentration is only 0.71%, which can be neglected. During the process of dual-alkali FGD, pH value of the absorbent is about 5.00~9.00 in validating the neglectation. Therefore, reaction (6) can be rewritten as

$$\text{TOS} = [\text{HSO}_3^-] + [\text{SO}_3^{2-}]. \quad (17)$$

The sulfite concentration can be derived from Eqs. (2), (9), (15)~(17):

$$[\text{SO}_3^{2-}] = ([\text{Na}^+] + [\text{H}^+] + 2[\text{Ca}^{2+}] - [\text{OH}^-]) \left(2 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}{K_{a1}K_{a2}} \frac{x}{1-x} \right)^{-1}. \quad (18)$$

And the capability of the solution is given by

$$\begin{aligned} \text{CS} &= [\text{SO}_3^{2-}] + [\text{OH}^-] = \\ &([\text{Na}^+] + [\text{H}^+] + 2[\text{Ca}^{2+}] - [\text{OH}^-]) \left(2 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}{K_{a1}K_{a2}} \frac{x}{1-x} \right)^{-1} + [\text{OH}^-]. \end{aligned} \quad (19)$$

The ability of desulfurization of the absorbent is equal to the product of absorbent flux and the total concentration of sulfite ion and hydroxide ion, which can be defined as *LCS*. The total sulfur dioxide in the flue gas is equal to the product of flue gas flow rate and the sulfur dioxide concentration of inlet flue gas, GC_{SO_2} . An indexing ε , defined as the ratio of the ability of desulfurization to the total sulfur dioxides was introduced into the system:

$$\begin{aligned} \varepsilon &= \frac{\text{LCS}}{GC_{\text{SO}_2}} = \frac{L}{G} \frac{\text{CS}}{C_{\text{SO}_2}} = \left[\frac{L}{GC_{\text{SO}_2}} \right] \\ &\left\{ ([\text{Na}^+] + [\text{H}^+] + 2[\text{Ca}^{2+}] - [\text{OH}^-]) \left(2 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}{K_{a1}K_{a2}} \frac{x}{1-x} \right)^{-1} + [\text{OH}^-] \right\}. \end{aligned} \quad (20)$$

Generally, pH value of the absorbent solution is higher

than 5.0, the concentrations of hydrogen ion and hydroxide ion compared with $[\text{Na}^+]$ (0.1~1.0 mol/L) are very small and can be neglected. Simultaneously, the calcium ion concentration (2~5 mmol/L) can also be assumed to be zero because of the very low solubility of calcium sulfite^[13]. Therefore, Eq.(20) can be written as

$$\varepsilon = \left(\frac{L}{GC_{\text{SO}_2}} \right) [\text{Na}^+] \left(2 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}}{K_{a1}K_{a2}} \frac{x}{1-x} \right)^{-1} \quad (21)$$

From the experimental study, increasing $[\text{Na}^+]$, L/G , pH value can promote desulfurization, but increasing sulfur dioxide content of inlet gas, temperature and x will reduce desulfurization. The results indicate that the variation trends of η and ε with five operating parameters are similar, and η is a function of ε .

From Fig.8 it can be seen that desulfurization efficiency increases with the increase in ε . When ε is below 10.0~20.0, the efficiency η increases rapidly at different temperatures. At the same ε , lower temperature leads to higher η .

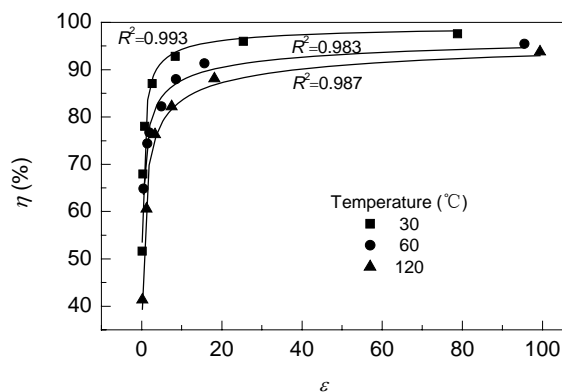


Fig.8 Relationship between η and ε

An empirical expression is concluded and can be written as

$$\eta = 100 \left[1 - \frac{1}{(1 + a\varepsilon)^{1/b}} \right], \quad (22)$$

where a is the parameter determined by the temperature and b determined by mass transfer conditions such as contact area, contact time and atomized conditions. The values of a and b are listed in Table 2.

Table 2 The parameters a and b at different temperatures

Parameter	30 °C	60 °C	120 °C
a	15.66	30.18	12.58
b	1.792	2.722	2.687

When ε is equal to 1.0, that means the ability of desulfurization of absorbent is equal to the amount of sulfur dioxide, η is 79.2%, 71.7% and 62.1% at 30, 60 and 120 °C, respectively. ε is required to be 13.6, 115.3 and 249.0 if η demands 95% at the 30, 60 and 120 °C, respectively. To get higher desulfurization efficiency, the desulfurization cost will increase greatly.

At a certain temperature, η can be determined by Eq.(21), and ε determined by the five operating parameters. For a desired value of ε , an optimal operating condition can be obtained from Eq.(21) which makes the best economic benefit. This expression has been applied in a 220 t/h boiler in Xuzhou, Jiangsu Province, which has achieved about 90% desulfurization efficiency.

4 CONCLUSIONS

The effects of main operating parameters (the concentration of sodium ion, the ratio of the absorbent flow rate to the gas flow rate, the pH of the absorbent, the ratio of sulfate ion to total sulfur and the sulfur dioxide concentration of inlet flue gas) on desulfurization efficiency of a dual-alkali FGD process in a RST scrubber has been investigated.

The dimensionless index ε is a function of five operating parameters and expresses the desulfurization ability of the absorbent. The expressions suggest that L/G and $[\text{Na}^+]$ are in direct proportion to ε while sulfur dioxide concentration of inlet flue gas is in inverse proportion to ε , which is in agreement with the experimental results.

The expression of desulfurization efficiency at different temperatures, Eq.(22), is correlated, and η is a function of ε and determined by temperature and mass transfer conditions. It shows that when ε value is lower than 10.0~20.0, η increases greatly with ε , while when ε is larger than 10.0~20.0, η increases slowly with ε . The optimal value of ε is 10~20 at which the desulfurization efficiency can reach 85%~95%. It can provide useful guide for engineering design.

Temperature has significant effect on the desulfurization efficiency when ε is greater than 1.0. Increasing the temperature will lower the desulfurization efficiency. However, the effect is minor when ε is lower than 1.0.

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