



Oxidation inhibition of sulfite in dual alkali flue gas desulfurization system

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Abstract

A laboratory-scale well-mixed thermostatic reactor with continuously blasting air was used to investigate the oxidation inhibition of sulfite in dual alkali flue gas desulfurization (FGD) system. The effects of operating parameters such as pH value and catalyst concentration on the oxidation were studied. Sodium thiosulfate was used in the system, and was found that it significantly inhibited the sulfite oxidation. In the absence of catalyst, sodium thiosulfate at 12.67 mmol/L had an inhibition efficiency of approximately 98%. While in the presence of catalyst, sodium thiosulfate at 26.72 mmol/L had an inhibition efficiency less than 85.0%. The oxidation reaction order of sulfite in the sodium thiosulfate was determined to be -1.90 and -0.55 in the absence and presence of the catalyst, respectively. Apparent activation energy of oxidation inhibition was calculated to be 53.9 kJ/mol. Pilot tests showed that the consumption rate of thiosulfate agreed well with the laboratory-scale experimental results.

Key words: dual alkali; sodium sulfite; oxidation inhibition; sodium thiosulfate

Introduction

Due to the oxidation reaction between the sulfite/bisulfite and dissolved oxygen, sulfate can be produced both in the lime and limestone flue gas desulfurization (FGD) system. In the presence of calcium ion, sulfate in the absorbent liquid will lead to the production of calcium sulfate, which is the main component of scaling and fouling. Accordingly, the reliability of the FGD system will be lowered. During regeneration step of dual alkali FGD system, sodium sulfate will react with lime and produce calcium sulfate and sodium hydroxide. And because of the high hardness of calcium sulfate, the absorbent liquid need to eliminate the hardness in a second sedimentation tank by sodium carbonate. One reason for the problem is that the boilers tend to be operated at higher levels of excess air. Another one is that the heavy metals in absorbent such as manganese, cobalt, and copper catalyze the oxidation rate. So oxidation inhibition is necessary for dual alkali FGD system to improve the reliability.

Uncatalyzed oxidation and catalyzed oxidation were investigated both in homogeneous and heterogeneous system in a review (Linek and Vacek, 1981). It is found that the oxidation rate of sulfite can be expressed as:

$$R = k C_{S(IV)}^{3/2} C_M^{1/2} C_{O_2}^0$$

where, R is the oxidation rate, k is the reaction constant,

$C_{S(IV)}$ is the concentration of S_{IV} , C_M is the concentration of catalyst and C_{O_2} is oxygen pressure. The parameters such as oxygen concentration and sulfite concentration were confirmed consistently both in homogeneous and heterogeneous system by theoretical and experimental studies. However, there are few works have been done on the effect of the catalyst concentration and pH value on oxidation rate.

Sodium thiosulfate was demonstrated to be an effective oxidation inhibitor, which is widely used in industry. Pilot tests were made on sodium thiosulfate oxidation inhibition in the sodium sulfite/bisulfite solution for a limestone regenerated dual alkali system (Chang and Kaplan, 1983). The successful application had been performed in a magnesium-enhanced lime system at the Philips Station of Duquesne Light. TVA Shawnee Station tested sodium thiosulfate in a prototype spray tower. It was found that only 100 mg/m³ of thiosulfate was needed to reduce the sulfate saturation and scale-free operation (Chang and Brna, 1986). Chang and Brna (1986) found that the concentration of thiosulfate ion from 100 to 200 mg/m³ could effectively avoid scaling. And it was also concluded that the consumption rate to achieve the oxidation inhibition effect should be in the range of 1 to 3 mmol Na₂S₂O₃/mol SO₂ absorbed both in lime and limestone systems. Later sulfur instead of sodium thiosulfate as an inhibitor has been studied for commercial purpose (Owens *et al.*, 1988). Thiosulfate was produced by sulfur reacting with the sulfite. Because of the low solubility of sulfur, the conversion of the sulfur to thiosulfate was not very high. Phenolic compounds were also known as

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effective inhibitors for the oxidation in both of organic and inorganic, but it is harmful to human health and hostile to the environment. They act as chain breakers by receiving excess energy from a "hot chain molecule" (Jeu and Alyen, 1933), or by scavenging free radicals, transients in a chain reaction (Huie and Neta, 1985). Wanda *et al.* (2003) explained the inhibition mechanism during the process of the removal of quinine. It was known from their work that the reaction transient acted as a catalyst, which transformed sulfite into sulfonates in the reaction. Most of these works focused on the oxidation and oxidation inhibition by thiosulfate in the lime or limestone slurry or in high diluted sulfite solutions. In this paper, we studied the influence of catalyst concentration and pH value on sulfite oxidation, sulfite oxidation inhibition by thiosulfate, the optimal parameters and the consumption rate of the inhibitor in concentrated solutions.

1 Materials and methods

The oxidation inhibition rate of sodium sulfite was determined with a laboratory scale apparatus in Fig.1. It consists of a thermostatic stirred reactor with feeding and discharging of gas phase. The liquid phase was kept in the reactor. The reactor, made of Pyrex glass, is a five-necked flask, the center neck for stirring, one pair necks for gas in and out, one for pH value measurement and the last for sampling. The volume of the reactor is 1000 cm³. An air compressor blasts air into the reactor continuously.

Since the sulfite oxidation was very sensitive to the impurities, distilled water and analytical grade of chemicals were used for all experiments. Even though it was treated carefully, there was still a little difference in the initial concentration of sulfite solution (approximately 25 mmol/L). The sodium ion concentration was about 50 mmol/L, which was very little compared with the sodium ion concentration (more than 1 mol/L) of typical dual alkali FGD system in US (Wang *et al.*, 1983; Pike, 1982). Dual-alkali FGD system in China is different from other countries, it only has single loop while others have two loops (Yan *et al.*, 1998; Li and Tan, 1999; Wu *et al.*, 2001). The sodium sulfite solution with sodium thiosulfate in the flask was rapidly and continuously stirred by a motor and bubble aerated by the air compressor. As soon as the stir and aeration began, the oxidation started and the pH value began to decrease. The rotating speed (*N*) was 350 r/min and the air compressor blast volume rate (*G*) was 180 L/h,

the temperature (*T*) was controlled at 25–55°C. A complex pH electrode connected to pH value measurement instrument (PHS-25) was used. The experiments were carried out both in the absence of catalyst and in the presence of manganese sulfate. The concentration of catalyst varied in the range of 1.0×10^{-6} – 5×10^{-3} mol/L. The concentration of 5 mmol/L was a high level for catalyst, and it was measured in the wastewater of desulfurization system in Hangzhou Banshan Power Plant. The pH value was controlled below 10.0. It was found that when pH was higher than 10.2, the catalysis will change from acceleration to deceleration of the oxidation rate (Lim and Hamrick, 1984).

The concentrations of sodium sulfite and sodium thiosulfate in the concentrated solution were measured analytically by means of an oxidation-reduction titration as the following: (1) a certain amounts of sulfite solution and thiosulfate was added to an excess of iodine-iodide standard solution which was then back titrated with 0.01 mol/L of sodium thiosulfate in arsenous acid solution with starch as an indicator; (2) the concentration of thiosulfate was analyzed directly by formaldehyde fixation of sulfite followed by iodine-iodide oxidation and back titration of excess iodine with arsenous acid. The concentration of sulfite was estimated as the difference between results obtained from (1) and (2).

2 Results and discussion

Oxidation inhibition of sulfite was investigated by adjusting the parameters: such as pH value, catalyst concentration, adding inhibitor in the dual-alkali FGD system. The mechanism of the oxidation inhibition and the operating parameters of inhibition process were focused on. Furthermore, the experimental consumption rate of inhibitor was also investigated and compared with the result of pilot test.

2.1 Effect of pH value

Fig.2 shows the oxidation process at 25°C without catalyst and controlling the pH value. In Fig.2 it was found that the plot of the sulfite concentration vs. time was a straight line with a slope of 15.38 mmol/(L·h) between 0 min to 80 min, which meant that the oxidation rate was constant with a pH value range from 6.4 to 8.9.

Fig.3 gives the results of a further study on the pH effect when pH was maintained constantly using 0.1 mol/L NaOH or 0.1 mol/L HCl. The results showed that the uncatalyzed oxidation rate increased from 7.956 to 17.90 mmol/(L·h) with an increase in pH value from 3.0 to 6.0. While it remained nearly constant with pH value kept within 6–8, only decreased about 3.0% from 17.90 to 17.36 mmol/(L·h).

Compared with the data in literature, the results at low pH value are similar to those of the former researchers. Wilkinson *et al.* (1993) found that the reaction rate decreased abruptly at low pH value (4.5–5.9), while the oxidation rate became constant with pH value above 5.9. Vidal and Ollero (2003) found that in the range of 2.0–6.0 of pH value, the oxidation rate was proportional to

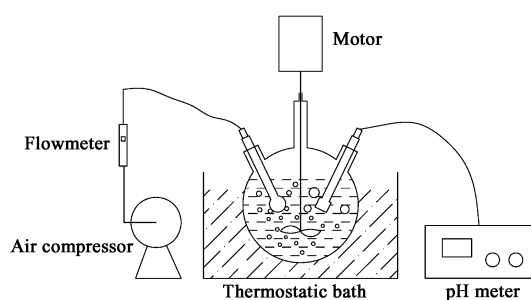


Fig. 1 Sketch of the experimental apparatus.

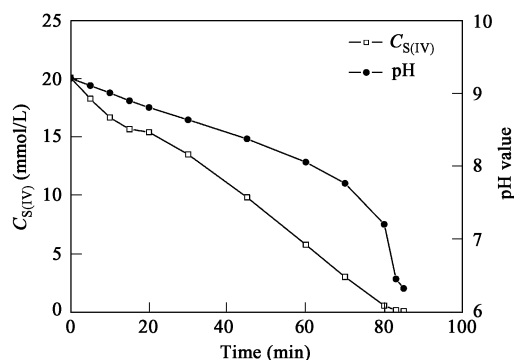


Fig. 2 Change of sulfite concentration ($C_{S(IV)}$) and pH with time. Temp.: 25°C; rotating speed: 100 r/min; rate: 180 L/h.

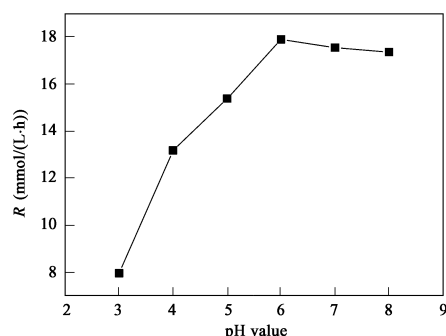


Fig. 3 Uncatalyzed oxidation rate (R) vs. pH value. Conditions are the same as Fig. 2.

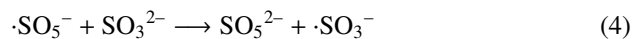
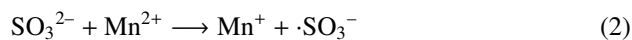
$C_{H^+}^{-0.69}$ in seawater. However, in the range 6.0–10.0 the oxidation rate began to decrease rapidly with pH value because of the conversion of acceleration to deceleration effect of the catalyst (Lim and Hamrick, 1984). Bengtsson and Bjerle (1975) found that the cobalt catalyzed oxidation rate was approximately proportional to $C_{OH^-}^{0.8}$ within the pH value range of 6.0–8.5 in dilute solution. The difference of the relation between the oxidation rate and pH value was the pH value range. The possible impact factors might be involved in system temperature, sulfite concentration, catalyst species, and mass transfer conditions. The oxidation rate increased with pH value can be explained by the relation between the sulfite and bisulfite as follows:



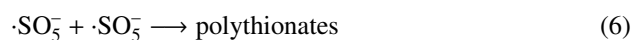
The oxidation rate is independent of the bisulfite concentration in homogeneous system. At low pH value, the main S(IV) exists as HSO_3^- , the concentration of SO_3^{2-} is low and the oxidation rate of sulfite becomes low. Increasing the pH value of the solutions gives a rise of the concentration of SO_3^{2-} and improves the oxidation rate of sulfite. However, when pH value is higher than 6, the sulfite concentration is so high that a further increase in the sulfite concentration contributes no more effect on the oxidation rate. In order to avoid the oxidation and improve the desulfurization rate, the pH value should be controlled at a lower value.

2.2 Effect of catalyst

The catalyzed oxidation reaction of sulfite to sulfate was regarded as a free-radical chain mechanism by several investigators in Linek's review (Linek and Vacek, 1981):



Step (4) is rapid and does not limit the over all reaction rate because of the zero order of the reaction with respect to oxygen in homogeneous systems. The termination occurs primarily by the combination:



The sulfite concentration in dual-alkali FGD system is relatively higher compared with that in the former research, about 25 mmol/L. The results in Fig. 4 show that the oxidation rate is nearly constant, 16.28 mmol/(L·h), in the range from 10 to 25 mmol/L of sulfite concentration. Compared with the oxidation rate without catalyst, the oxidation rate increased about 5.8% from 15.38 to 16.28 mmol/(L·h) at pH=5. The reaction rate is independent of the catalyst concentration in high sulfite concentration solution, which means that the reaction is zero order with respect to catalyst concentration. The result differs from the former researchers' results because that the oxidation reaction takes place in three different regime: kinetic, diffusional and fast reaction regime. When the process takes place in the diffusional regime, the overall reaction rate is independent on liquid-phase composition, and it is only controlled by the mass transfer of oxygen (Danckwerts, 1970; Lancia *et al.*, 1999).

2.3 Effect of the sodium thiosulfate

Sodium thiosulfate inhibits the oxidation rate both in the absence of manganese sulfate and in the presence of 5 mmol/L manganese sulfate as shown in Fig. 5. The presence of sodium thiosulfate in the solution decreases the oxidation rate evidently both in the absence of manganese

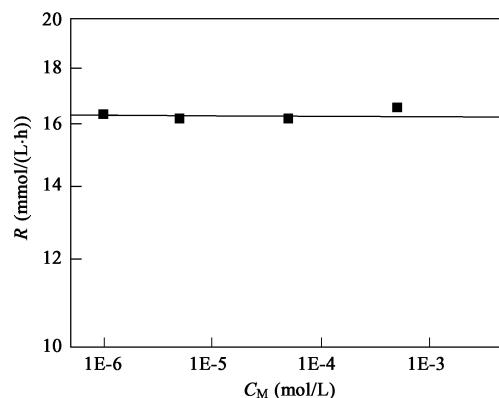


Fig. 4 Catalyzed oxidation rate (R) vs. catalyst concentration (C_M). Conditions are the same as Fig. 2.

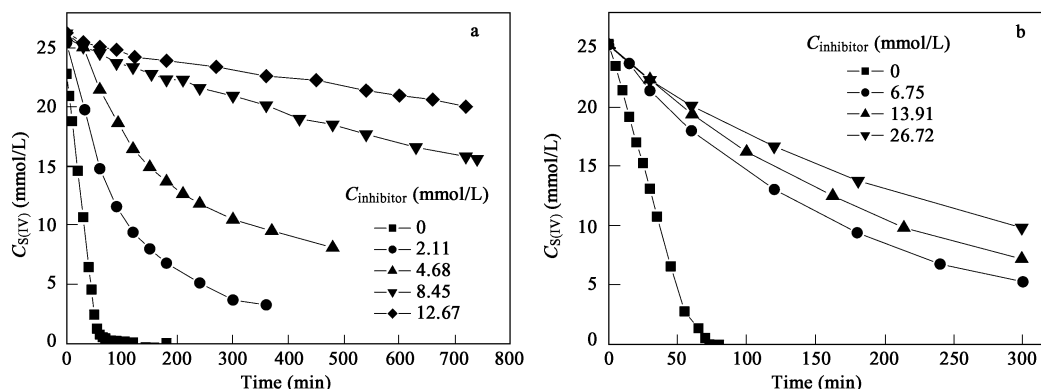
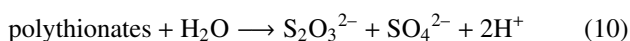
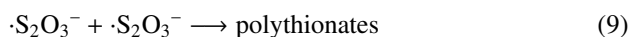
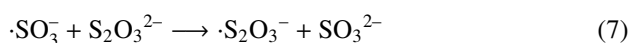


Fig. 5 Sulfite oxidation inhibition ($C_{S(IV)}$) vs. time at different inhibitor concentration in uncatalyzed oxidation process (a) and catalyzed oxidation process (b). Temp. 25°C; rotating speed 350 r/min; rate 180 L/h; $C_{MnSO_4} = 5.0 \times 10^{-3}$ mol/L.

sulfate and in the presence of manganese sulfate. The mechanisms of the inhibition effect of thiosulfate can be explained as follows (Chang and brna, 1986):



Thiosulfate acts as a free radical scavenger, which scavenges the $\cdot SO_3^-$ producing from Reaction (2) and breaks the chain Reaction (3).

From Figs. 5a, b, it can be found that the concentration of sulfite began to decrease rapidly with a steep line without inhibitor both in the absence of catalyst and in the presence of catalyst. Fig. 5a shows that sodium thiosulfate could markedly reduce the oxidation rate in the absence of catalyst at a relatively low thiosulfate concentration of 2.11 mmol/L. The oxidation inhibition efficiency increases with sodium thiosulfate concentration. When the sodium thiosulfate was about 8.45 mmol/L, the oxidation rate of sulfite was nearly constant. The oxidation rate of sulfite is 0.374 mmol/(L·h) in the presence of sodium thiosulfate at 12.67 mmol/L, the oxidation inhibition efficiency is 97.6%. Fig. 5b shows that the oxidation inhibition of sulfite in the presence of catalyst was more difficult to carry out than

that in the absence of catalyst. The oxidation rate inhibition efficiency reached only about 85% at relatively high inhibitor concentration of 26.72 mmol/L. Increasing the concentration of inhibitor contributed little to the inhibition efficiency at high concentration both in the absence or presence of catalyst.

The inhibition process in the absence of catalyst is dependent on the inhibitor concentration at relatively low inhibitor concentration ($C_{inhibitor} < 12.67$ mmol/L). And the same phenomena occurs in the presence of catalyst at relatively high inhibitor concentration ($C_{inhibitor} < 26.72$ mmol/L). The processes take place in the kinetic regime. From Fig. 6a, it can be known that all the experimental data are fitted well with a -1.90 reaction order with respect to inhibitor concentration during the uncatalyzed oxidation process, while the corresponding value is -0.55 during the catalyzed oxidation process from Fig. 6b.

2.4 Consumption rate of the inhibitor

Air oxidation of thiosulfate under normal pressures and temperature was a very slow process (Dinegar *et al.*, 1991; Rolla and Chakrabarti, 1982). The experimental results show that the self-oxidation of thiosulfate could be ignored at pH=6 and pH=12 in the absence of catalyst or not. The oxidation inhibition process has an induction time as shown in Figs. 7a, b. The induction time was approximately 1 h in the absence of catalyst and half an hour in the

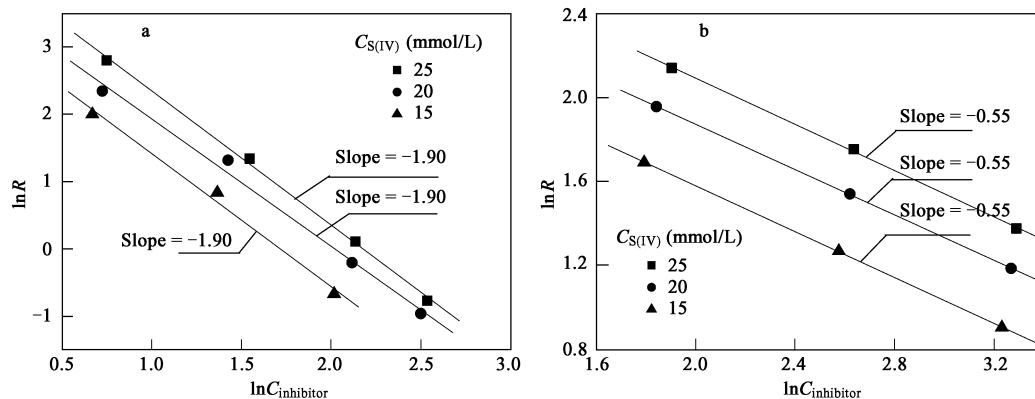


Fig. 6 Uncatalyzed oxidation rate (a) and catalyzed oxidation rate (b) as a function of the concentration of sodium thiosulfate. Conditions are the same as Fig. 5.

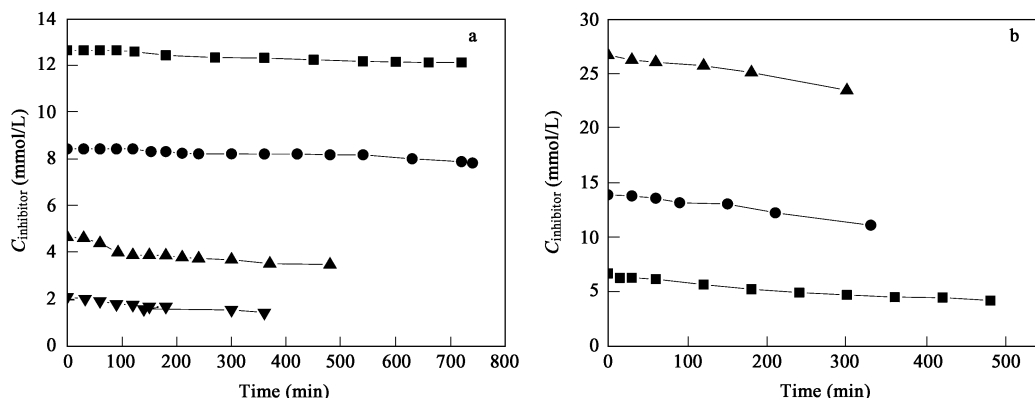


Fig. 7 Thiosulfate concentration varies with time in the absence (a) and presence (b) of catalyst. Conditions are the same as Fig.5.

presence of catalyst. The consumption of thiosulfate is because that not all the polythionates can reaction with water (see Equation (10)). The average consumption rate of thiosulfate was approximately 6.00×10^{-2} mmol/(L·h) in the absence of catalyst although the initial concentration is different. But the corresponding value reached as high as 4.80×10^{-1} mmol/(L·h) in the presence of catalyst. The ratio of inhibitor consumption rate to the sulfite oxidation rate is 4.00 and 30.00 mmol $\text{Na}_2\text{S}_2\text{O}_3$ /mol Na_2SO_3 in the absence of catalyst and presence of catalyst respectively.

2.5 Activation energy

With concentrated sulfite and inhibitor concentration at 12.67 mmol/L solution, the reaction rate was determined to be 25, 35, 45 and 55°C at pH=6. Activation energy (E_a) can be determined by the slope of $\ln k$ and $(-1/RT)$ according to the Arrhenius equation:

$$\ln k = A_0 - \frac{E_a}{RT} \quad (11)$$

where k is the reaction rate constant, A_0 is index factor, R is gas constant and T is temperature. The plot of $\ln k$ against the reciprocal of absolute temperature is shown in Fig.8. The apparent activation energy of 53.9 kJ/mol was determined from the slope of the straight line. This value is close to the oxidation reaction activation energy from the literature: 53.5 kJ/mol (Linek and Mayrhoferova, 1970) and 50 kJ/mol (de Waal and Okeson, 1966).

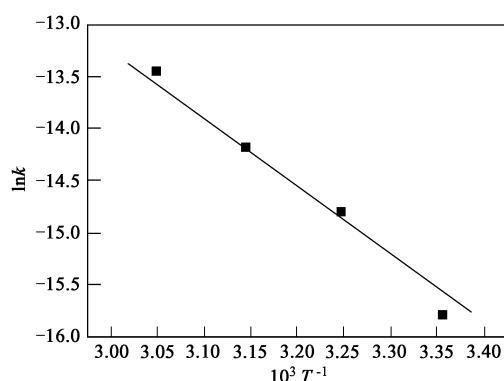


Fig. 8 Temperature dependency of the zero order reaction rate constant at pH=6.0 and $C_{\text{inhibitor}}=1.27 \times 10^{-2}$ mol/L in concentrated solution.

2.6 Industrial test

Dual-alkali (Na-Ca) flue gas desulfurization was carried out in rotating-stream-tray (RST) scrubber. The flue gas was dust removed and desulfurized simultaneously with a RST scrubber. The test conditions were in the following: scrubber's diameter (D): 300 mm; gas flow rate (G): 1000 m^3/h ; gas temperature (T): 180°C; C_{SO_2} : 500 ppm; L/G : 1–3 L/m^3 ; C_{Na^+} : 0.05 mol/L; $C_{\text{Na}_2\text{S}_2\text{O}_3}$: 6.25 mmol/L. The results show that desulfurization efficiency was approximately 90%–95%, which is 5%–10% higher compared with that without inhibitor. When pH value was maintained at 5.6–8.0, active sodium was maintained at about 20 mmol/L. The consumption rate of thiosulfate was approximately 30.00 $\text{Na}_2\text{S}_2\text{O}_3/\text{SO}_2$. The consumption rate was equal to the result in the presence of catalyst experiment, because the fly ash including metal ions, which have catalytic effect, are dissolved in the solutions. According to the results of industrial test, the addition of sodium thiosulfate to the dual-alkali system will lead to an increase in operating cost about 60 RMB Yuan/t SO_2 . It is approximately 7.5% higher than the operating cost without inhibitor (800 RMB Yuan/t SO_2). Therefore, the operating cost is still acceptable.

3 Conclusions

Oxidation of sodium sulfite in concentrated solution is dependent on the pH value and independent on the catalyst concentration in diffusional regime. In order to avoid the oxidation, a low pH value is recommended.

Sodium thiosulfate has good inhibition effect on sulfite oxidation. In the absence of catalyst, the oxidation efficiency can reach 97.6% when sodium thiosulfate is 12.67 mmol/L. In the presence of catalyst, only 85.0% of the oxidation efficiency can be obtained even the concentration of sodium thiosulfate is 26.72 mmol/L. The oxidation reaction order of sulfite in the sodium thiosulfate is determined to be -1.90 in the absence of the catalyst and -0.55 in the presence of the catalyst, respectively.

According to the experimental results, the consumption rate of thiosulfate is 4.00 and 30.00 mmol $\text{Na}_2\text{S}_2\text{O}_3$ /mol Na_2SO_3 in the absence of catalyst and in the presence of catalyst, respectively.

RST scrubber test shows that the sodium thiosulfate can enhance the desulfurization efficiency in dual-alkali FGD system and the consumption rate of thiosulfate is in well agreement with experimental results (approximately 30.00 mmol $\text{Na}_2\text{S}_2\text{O}_3/\text{mol SO}_2$) in the presence of catalyst.

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