ELSEVIER

Chemical Engineering Journal 136 (2008) 221–226

Chemical Engineering Journal

www.elsevier.com/locate/cej

Kinetics of sulfite oxidation in wet desulfurization with catalyst of organic acid

Lidong Wang*, Yi Zhao*

School of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China

Received 19 July 2006; received in revised form 20 March 2007; accepted 1 April 2007

Abstract

Catalytic effects of nine organic acids on the oxidation of sulfite were compared, in which peracetic acid was the most effective. The intrinsic oxidation kinetics of sodium sulfite catalyzed by peracetic acid were studied using intermittent apparatus, and reaction orders of the reagents and activation energy obtained. Using bubbling apparatus, the macroscopic catalyzed oxidation kinetics of calcium sulfite were investigated by varying pH, concentration of calcium sulfite and peracetic acid, airflow flux and temperature. A mathematical model was established that involved intrinsic reaction, dissolution of calcium sulfite and diffusion of oxygen. It was concluded that the macroscopic reaction is controlled by diffusion of oxygen, which benefits wet flue gas desulfurization.

Keywords: Kinetics; Sulfite; Oxidation; Peracetic acid; Catalyze; Wet desulfurization

---

1. Introduction

Sulfur dioxide is a major air pollutant that has attracted much attention. Oxidation of calcium sulfite is of great importance in wet flue gas desulfurization, with forced oxidation being a particularly popular application. During forced oxidation, a blower injects air into the slurry, oxidizing the sulfite into sulfate. However, due to the low oxidation rate, most of the air is wasted, resulting in excess investment and energy. Furthermore, jams and accumulation of filth also frequently occur during practical application.

On the basis of uncatalyzed oxidation kinetics [1–5], the effects of transition metal ions such as manganese, copper, cobalt and ferrous on the oxidation rate of sulfite have been thoroughly investigated [6–14]. In addition, we also revealed many inhibitors that slow down the oxidation process [15]. These results show that oxidation of sulfite is a chain reaction initiated by metal ions.

There are two kinds of kinetics, intrinsic and macroscopic. The former is used to study the mechanisms of chemical reactions, which are usually carried out under homogeneous conditions, while the latter consider not only the chemical reaction, but also mass transfer of reagents between different phases, which are often carried out under heterogeneous conditions. In wet desulfurization, the oxidation of sulfite accompanies mass transfer, which, as mentioned above, is a macroscopic process.

Unfortunately, most published work concentrates on the catalytic effect of transition metal ions. That of organic acid, which is cheaper and causes less secondary pollution, however, has yet to be investigated. In the present work, nine organic acid catalysts [16,17] were screened and, of these, macroscopic oxidation results revealed that peracetic acid was the best catalyst. In the presence of peracetic acid, the intrinsic oxidation kinetics of sodium sulfite were subsequently studied using intermittent apparatus. Using experimental parameters close to the practical setting, the macroscopic catalyzed oxidation kinetics of calcium sulfite were then studied using bubbling apparatus. Based on the intrinsic kinetics, a mathematical model of the macroscopic process was thereby established and the controlling rate step deduced. In this way, the catalyzed mechanism was confirmed, thus benefiting the exploration of new cheap and effective additives for forced oxidation in wet flue gas desulfurization.

2. Experimental

2.1. Experiment of the intrinsic reaction kinetics

Intermittent apparatus was used to analyze the intrinsic reaction kinetics. Briefly, a known quantity of distilled water and

---

* Corresponding authors. Tel.: +86 312 7522343.
E-mail addresses: wld@ncepubd.edu.cn (LD. Wang), zhaoyi9515@163.com (Y. Zhao).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.04.004

Nomenclature

C_A	concentration of oxygen in the solution ($mol\,L^{-1}$)
C_{Ai}	equilibrium concentration of oxygen at the interphase ($mol\,L^{-1}$)
C_B	concentration of calcium sulfite particles in solution ($mol\,L^{-1}$)
C_S	saturation concentration of calcium sulfite particles in solution ($mol\,L^{-1}$)
$C_{S(IV)t}$	concentration of sulfate at time t ($mol\,L^{-1}$)
$C_{S(IV)0}$	initial concentration of sulfate ($mol\,L^{-1}$)
C_1	concentration of sulfite ($mol\,L^{-1}$)
C_{1t}	concentration of sulfite at time t ($mol\,L^{-1}$)
C_{2t}	concentration of dissolved oxygen at time t ($mol\,L^{-1}$)
$C_{1\,0}$	initial concentration of sulfite ($mol\,L^{-1}$)
$C_{2\,0}$	initial concentration of dissolved oxygen ($mol\,L^{-1}$)
C_3	concentration of peracetic acid ($mol\,L^{-1}$)
D	diffusion coefficient of calcium sulfite ($m^2\,s^{-1}$)
D_A	diffusion coefficient of oxygen in the solution ($m^2\,s^{-1}$)
E_a	activation energy ($kJ\,mol^{-1}$)
f_2	function between C_{2t} and t
k	coefficient of intrinsic reaction rate ($mol^{-1.5}\,L^{1.5}\,s^{-1}$)
k_{a1}	ionization constant of the first step
k_{a2}	ionization constant of the second step
m	reaction order of oxygen in the intrinsic reaction
M	amount of froth in unit time
n	reaction order of sulfite in the intrinsic reaction
N	amount of balls that was proportional to initial quantity of calcium sulfite
Q	volume of injected air in unit time (m^3)
r_j	radius of balls (m)
R	macroscopic reaction rate ($mol\,L^{-1}\,s^{-1}$)
R_A	intrinsic reaction rate ($mol\,L^{-1}\,s^{-1}$)
R_B	dissolution rate of calcium sulfite ($mol\,L^{-1}\,s^{-1}$)
R_C	diffusion rate of oxygen ($mol\,L^{-1}\,s^{-1}$)
R_M	diffusion rate of oxygen in single froth ($mol\,L^{-1}\,s^{-1}$)
t	reaction time (s)

Greek letter

δ_0	distribution coefficient of sulfite ions $SO_3{}^{2-}$

trace quantity of organic acid were added to the reactor. After fixing a dissolved oxygen probe in the solution, the reactor was sealed and placed in a water bath. The rotation speed was adjusted to a scheduled value, and the reaction was started at the same time as sodium sulfite solution was added to the reactor to a total volume of 1.0 L. The concentration of dissolved oxygen was recorded during the reaction process, and using this, the sulfite concentration could be obtained at any time as follows:

$$SO_3{}^{2-} + 1/2O_2 \rightarrow\ SO_4{}^{2-} \tag{1}$$

$$\begin{array}{lll} \text{initial time}: & C_{10} & C_{20} \\ t: & C_{1t} & C_{2t} \end{array}$$

The statistical software SPSS was used for regressive analysis of the experimental data, and the relationship between the dissolved oxygen concentration and reaction time was determined as $C_{2t} = f_2(t)$. Thus, the intrinsic reaction rate at any time was given by $2\,df_2(t)/dt$.

2.2. Experiment of the macroscopic reaction kinetics

Bubbling apparatus was used to analyze the macroscopic reaction kinetics. Briefly, 150 mL of distilled water was added to the reactor after adjusting the temperature, rotation speed of the stirrer and airflow velocity to scheduled values. Air was injected into the reactor after a known quantity of organic acid and calcium sulfite were added to the water. Solution of hydrochloric acid and ammonia were used to adjust the pH. The temperature, airflow velocity and pH were also observed and adjusted to the scheduled values during the course of the reaction. The production was dissolved by adding hydrochloric acid at the fixed time. The concentration of sulfate was then measured and the initialization involved in the sulfite removed. The concentration of sulfate was measured according to the turbidimetric method, and the observed oxidation rate was calculated using the following formula [2]:

$$R = \frac{C_{S(VI)t} - C_{S(VI)0}}{t} \tag{2}$$

For example, to screen the most effective catalyst, 1.00 g calcium sulfite was oxidized for 30 min under the following conditions: pH, 5.5; airflow flux, $0.056\,m^3\,h^{-1}$; organic acid, 3.55×10^{-4} mol; temperature, 27.0 °C.

2.3. Experimental reagents

The following reagents were used: anhydrous sodium sulfate, sodium sulfite, calcium sulfite, peracetic acid, formic acid, acetic acid, oxalic acid, hexanedioic acid, tartaric acid, salicylic acid, hydrogen peroxide, benzoic acid, hydrochloride acid, ammonia, sodium chloride, barium chloride, glycerol, and alcohol; all were of analytical purity grade. Solution of peracetic acid was prepared after leaving it to stand for 24 h then diluting it to 2% for the intrinsic reaction and 30% for the macroscopic reaction. The fixing reagent was composed of 75 g sodium chloride, 300 mL distilled water, 30 mL hydrochloride acid, 50 mL glycerol and 100 mL alcohol, mixed well. The standard sulfate solution was composed of 1.4787 g anhydrous sodium sulfate dissolved in 1000 mL distilled water.

3. Results and discussion

3.1. Organic acid screening

The effect of each organic acid is shown in Fig. 1. The results showed that peracetic acid was the best catalyst, probably because it initiated the free radical reaction and significantly

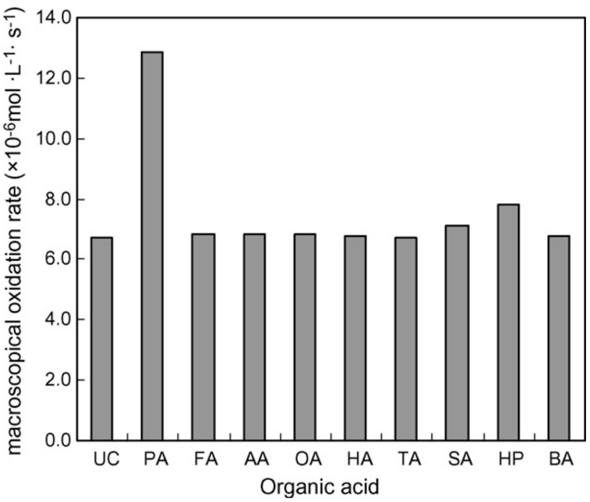

Fig. 1. Effect of organic acid on macroscopical oxidation of sulfite. UC: uncatalyzed; PA: peracetic acid; FA: formic acid; AA: acetic acid; OA: oxalic acid; HA: hexanedioic acid; TA: tartaric acid; SA: salicylic acid; HP: hydrogen peroxide; BA: benzoic acid.

improved the reaction rate (this will be discussed in Sections 3.2 and 3.3). However, hydrogen peroxide seemed to act as oxidant, though it was much less effective than peracetic acid. None of the other organic acids had a strong effect on the reaction rate, either as a catalyst or strong oxidant.

3.2. Results of intrinsic kinetics

According to Section 2.1, when the initial concentration of dissolved oxygen was 2.40×10^{-4} mol L^{-1} and the sodium sulfite concentration 6.00×10^{-3} mol L^{-1} at 24.0 °C, the effect of peracetic acid on the intrinsic reaction rate was as is shown in Fig. 2. The concentration of peracetic acid and reaction rate were made dimensionless with respect to the value, and the results show that the intrinsic oxidation rate was 1.0 order in concentration of peracetic acid (see Table 1).

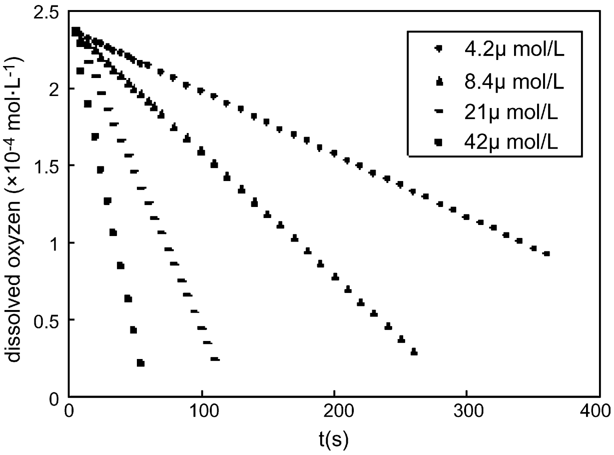

Fig. 2. Effect of peracetic acid concentration on intrinsic reaction rate.

Table 1
Reaction order of peracetic acid in intrinsic oxidation

	No.			
	1	2	3	4
C_3 (mol L^{-1})	4.20×10^{-6}	8.40×10^{-6}	2.10×10^{-5}	4.20×10^{-5}
r (mol L^{-1} s^{-1})	8.13×10^{-7}	1.63×10^{-6}	4.06×10^{-6}	8.50×10^{-6}
Relationship	$r \infty C_3$			

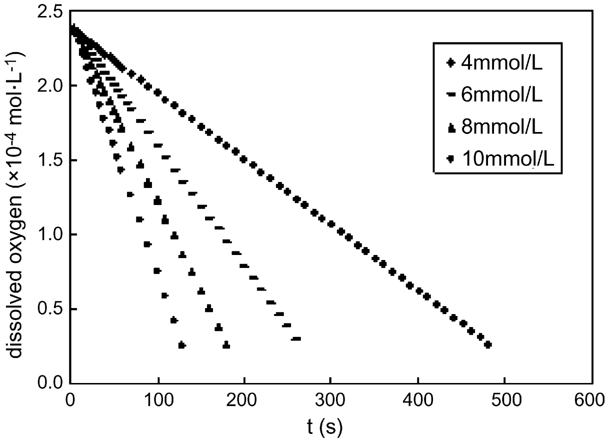

Fig. 3. Effect of sulfite concentration on intrinsic reaction rate.

When the initial concentration of peracetic acid was 8.40×10^{-6} mol L^{-1}, the effect of sodium sulfite on the intrinsic reaction rate under the same conditions was as is shown in Fig. 3. The concentration of sodium sulfite and reaction rate were made dimensionless with respect to the value, and the intrinsic oxidation was shown to be 1.5 order in concentration of sodium sulfite (see Table 2).

As shown in Fig. 3, while the concentration of sulfite, 1.0×10^{-2} mol L^{-1}, was much more than that of dissolved oxygen, there was only a trace amount of peracetic acid. Further, the concentration of dissolved oxygen decreased linearly with reaction time, indicating that the reaction order of dissolved oxygen was zero.

Using the above results, the following equation of the intrinsic reaction rate was obtained:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = kC_1^{3/2}C_3 \tag{3}$$

Fig. 4 shows the effect of temperature on the intrinsic reaction rate given initial concentrations of dissolved oxygen, sodium sulfite and peracetic acid of 2.40×10^{-4}, 6.00×10^{-3} and 8.40×10^{-6} mol L^{-1}, respectively. Using Eq. (3), when T = 14.0, 19.0, and 24.0 °C, k = 101, 208 and 416 mol$^{-1.5}$ L$^{1.5}$ s^{-1}, respectively. According to the Arrhenius equation $k = k_0\,\mathrm{e}^{-E_\mathrm{a}/RT}$, the activation energy, E_a, is about 101.6 KJ mol^{-1} and k_0 about 3.06×10^{20} mol$^{-1.5}$ L$^{1.5}$ s^{-1}.

Table 2
Reaction order of sodium sulfite in intrinsic oxidation

	No.			
	1	2	3	4
C_1 (mol L^{-1})	4.00×10^{-4}	6.00×10^{-4}	8.00×10^{-4}	1.00×10^{-3}
r (mol L^{-1} s^{-1})	8.81×10^{-7}	1.63×10^{-6}	2.42×10^{-6}	3.44×10^{-6}
Relationship	$r \infty C_1^{1.5}$			

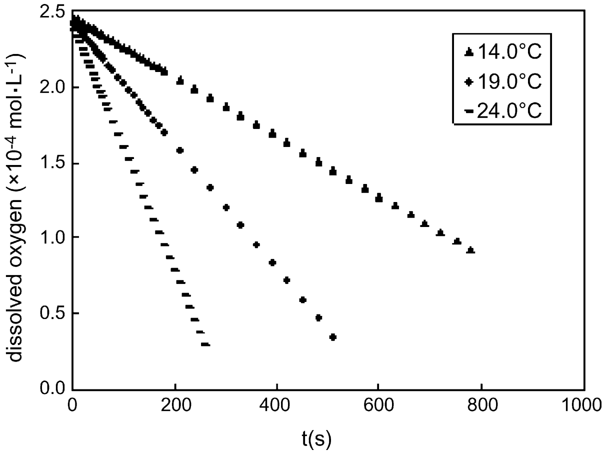

Fig. 4. Effect of temperature on intrinsic reaction rate.

Table 3
Effect of pH on macroscopical reaction rate

pH	R ($\times 10^{-6}$ mol L^{-1} s^{-1})
4.5	17.31
5.0	14.65
5.5	13.80
6.0	11.12

3.3. *Results of macroscopic kinetics*

According to Section 2.2, when the airflow flux was 0.056 m^3 h^{-1} and the peracetic acid concentration 4.50×10^{-3} mol L^{-1} at 27.0 °C, 1.00 g calcium sulfite was oxidized for 30 min. The effect of pH on the macroscopic reaction rate is shown in Table 3. The results indicate that the oxidation rate decreases with increasing pH.

Under the same conditions, Table 4 shows the effect of the initial concentration of calcium sulfite on the macroscopic reaction rate at pH 5.5. The results indicate that macroscopic oxidation is 0.1 order in concentration of calcium sulfite approximately.

The effect of airflow flux on the macroscopic reaction rate is shown in Table 5. When the airflow flux was between 0.032 and 0.080 m^3 h^{-1}, the bubbled air had little stirring effect on the reaction solution. Influenced by the stirrer, regular bubbling was observed and the air froth dispersed uniformly, resulting in a quiet bubbling area. When the airflow flux was increased to 0.104 m^3 h^{-1}, on the other hand, some air froth collided and agglomerated, resulting in a turbulent bubbling area. Table 5 shows that the macroscopic oxidation rate increases with a rise in airflow flux between 0.032 and 0.080 m^3 h^{-1}. When the airflow flux was increased further, however, the oxidation rate decreased.

Table 4
Effect of calcium sulfite on macroscopical reaction rate

Calcium sulfite (mol L^{-1})	R ($\times 10^{-6}$ mol L^{-1} s^{-1})
0.049	13.79
0.096	14.77
0.144	15.51
0.192	16.14
0.285	16.76

Table 5
Effect of airflow flux on macroscopical reaction rate

Airflow flux (m^3 h^{-1})	R ($\times 10^{-6}$ mol L^{-1} s^{-1})
0.032	12.62
0.056	13.80
0.080	15.00
0.104	14.75

Table 6
Effect of peracetic acid on macroscopical reaction rate

Peracetic acid ($\times 10^{-3}$ mol L^{-1})	R ($\times 10^{-6}$ mol L^{-1} s^{-1})
2.24	12.83
4.47	14.80
6.71	17.54
8.94	20.74

Table 7
Effect of temperature macroscopical reaction rate

Temperature (°C)	R ($\times 10^{-6}$ mol L^{-1} s^{-1})
27.0	13.80
35.0	15.87
43.0	17.59
51.0	18.45
60.0	19.40

Table 6 shows the effect of the initial concentration of peracetic acid on the macroscopic reaction rate, indicating that the macroscopic oxidation is 0.5 order in concentration of peracetic acid approximately. The effect of temperature is shown in Table 7, indicating an increase with increasing temperature.

4. Mechanism of macroscopic oxidation kinetics

The macroscopic oxidation process of calcium sulfite could be divided into three steps: an intrinsic reaction in the liquid phase, R_A, dissolution of calcium sulfite from solid particles into liquid, R_B, and mass transfer of oxygen into liquid, R_C.

4.1. *Intrinsic reaction rate R_A*

Calcium sulfite ($CaSO_3{\cdot}1/2H_2O$) barely dissolved in the reagent. Sulfurous acid ionizes in two stages as follows:

$$H_2SO_3 \leftrightarrow H^+ + HSO_3^-, \quad k_{a1} = 1.5 \times 10^{-2} \tag{4}$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}, \quad k_{a2} = 1.0 \times 10^{-7} \tag{5}$$

Thus, sulfite exists as SO_3^{2-}, HSO_3^- and H_2SO_3. The distribution coefficient of SO_3^{2-} is

$$\delta_0 = \frac{[SO_3^{2-}]}{c} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \tag{6}$$

At pH 5.5, δ_0 was 0.031, and the solubility of calcium sulfite was determined as

$$S_{\mathrm{CaSO_3}} = [\mathrm{Ca}^{2+}] = [\mathrm{SO_3}]_{\mathrm{total}} = \sqrt{\frac{K_{\mathrm{sp,CaSO_3}}}{\delta_0}}$$

$$= \sqrt{\frac{6.8\times 10^{-8}}{0.031}} = 1.48\times 10^{-3}\,\mathrm{mol\,L^{-1}} \qquad (7)$$

When the calcium sulfite saturated, the intrinsic oxidation rate could then be calculated using Eq. (3).

4.2. Dissolution rate of calcium sulfite R_B

In solution with a volume of V, calcium sulfite samples were assumed to form little balls equal in size and in amount of N, which was proportional to the initial quality. Accordingly, diffusion took place from the surface of the ball into the solvent at a rate of $(-4\pi r^2 D(\mathrm{d}C/\mathrm{d}r))$. According to the balance of materials, the sum of dissolved solute was equal to the increased concentration of solute in the solution:

$$V\frac{\partial C}{\partial t} = -4\pi r^2 DN\frac{\partial C}{\partial r} \qquad (8)$$

In the above equation, the boundary condition was as follows:

$$r = r_{\mathrm{j}}, C = C_{\mathrm{S}}; \qquad r = +\infty, C = C_{\mathrm{B}}$$

This resulted in

$$R_{\mathrm{B}} = \frac{\partial C}{\partial t} = \frac{4\pi D r_{\mathrm{j}} N}{V}(C_{\mathrm{S}} - C_{\mathrm{B}}) \qquad (9)$$

4.3. Diffusion rate of oxygen R_C

In the quiet bubbling area, it was assumed: (1) the air froth bubbles were equal in size and showed little agglomeration during the rise process; (2) the oxygen concentration in the single air froth remained constant. For example, as shown in Table 6, when the oxidation rate was $2.07\times 10^{-5}\,\mathrm{mol\,L^{-1}\,s^{-1}}$, the airflow flux and reaction time resulted in 0.263 mol bubbled oxygen. According to the produced sulfate, the reacted oxygen was 2.63×10^{-3} mol. This shows that the utility of oxygen was rather low, consistent with the assumption; (3) the pressure of the air froth remained constant during the rise process, and was equal to the atmospheric pressure. In the solution, the pressure of the air froth was $(P_0 + \rho g h)$, but since the height of reactor was relatively low, $(\rho g h)$ was neglected. The assumption mentioned above resulted in

$$Q = M\pi r_{\mathrm{g}}^3 \qquad (10)$$

$$R_{\mathrm{C}} = MR_{\mathrm{M}} = \frac{Q}{\pi r_{\mathrm{g}}^3} R_{\mathrm{M}} \qquad (11)$$

The diffusion rate was controlled by mass transfer in the liquid film. Also, taking into account the chemical reaction, the mass transfer rate of single air froth was determined according to the theory of double film:

$$R_{\mathrm{M}} = k'_{\mathrm{L}}(C_{\mathrm{Ai}} - C_{\mathrm{A}}) \qquad (12)$$

Further, as the chemical reaction was rapid, it was thus simplified to

$$k'_{\mathrm{L}} \approx \sqrt{\frac{2}{m+1} D_{\mathrm{A}} k C_{\mathrm{Ai}}^{m-1} C_{\mathrm{B}}^{n}} \qquad (13)$$

The concentration of oxygen measured in the reaction system was approximately zero giving:

$$R_{\mathrm{M}} = \sqrt{\frac{2}{m+1} D_{\mathrm{A}} k C_{\mathrm{Ai}}^{m-1} C_{\mathrm{B}}^{n}} \times C_{\mathrm{Ai}} = \sqrt{2 D_{\mathrm{A}} k C_{\mathrm{Ai}} C_{\mathrm{B}}^{1.5}} \qquad (14)$$

$$R_{\mathrm{C}} = \frac{Q}{\pi r^3}\sqrt{2 D_{\mathrm{A}} k C_{\mathrm{Ai}} C_{\mathrm{B}}^{1.5}} \qquad (15)$$

The catalytic effect of peracetic acid was regarded as a magnification of the reaction coefficient k, and was simplified as follows:

$$R_{\mathrm{C}} = \frac{Q}{\pi r_{\mathrm{g}}^3}\sqrt{2 D_{\mathrm{A}} k C_{\mathrm{Ai}} C_1^{1.5} C_3} \qquad (16)$$

It was concluded that the diffusion rate of oxygen was (1) proportional to the airflow flux; (2) inversely proportional to the cube of the radius of the air froth; (3) 0.75 order in dissolved sulfite; (4) 0.5 order in peracetic acid.

4.4. Macroscopic reaction rate R

As the above three steps proceed simultaneously, the macroscopic reaction rate depends on the slowest one:

$$R = \min(R_{\mathrm{A}}, R_{\mathrm{B}}, R_{\mathrm{C}}) \qquad (17)$$

Dissolution of calcium sulfite is an exothermic reaction; thus, if the macroscopic reaction rate is controlled by R_{B}, it should have decreased with the rise in temperature, which conflicts with the results shown in Table 7. It was therefore concluded that the dissolution of sulfite is not the controlling rate step, and that calcium sulfite reaches saturation rapidly due to quick dissolution. According to Section 4.1, the concentration of dissolved sulfite should be $1.48\times 10^{-3}\,\mathrm{mol\,L^{-1}}$ at pH 5.5.

According to Eq. (3), the coefficient of the intrinsic reaction rate k is $628\,\mathrm{mol^{-1.5}\,L^{1.5}\,s^{-1}}$. If the reaction rate is controlled by R_{A}, the intrinsic reaction rate should be $6.60\times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$ when the concentration of peracetic acid is $7.10\times 10^{-4}\,\mathrm{mol\,L^{-1}}$ at 27.0 °C. Table 6 shows that the macroscopic reaction rate is much lower than that of the intrinsic reaction rate, which therefore is not the controlling rate step either. Thus, it was concluded that the reaction is controlled by mass transfer of oxygen. Under heterogeneous conditions, this should occur as follows:

(1) According to Section 4.1, δ_0 is thought to decrease with a rise in pH, leading to an increase in the dissolved sulfite

concentration C_1. As shown in Eq. (16), the reaction rate is then expected to increase accordingly, consistent with the findings shown in Table 3.

(2) As shown in Eq. (16), the macroscopic reaction was 0.5 order in peracetic acid, which is consistent with Table 6.

(3) The concentration of calcium sulfite has little effect on the reaction rate; rather, due to quick dissolution, calcium sulfite is thought to become almost completely saturated in the solution.

(4) In the quiet bubbling area, as the radius of the air froth remains constant, the mass transfer rate increases with a rise in airflow flux. In the turbulent bubbling area, on the other hand, the radius of some air froth increases due to collision. According to Eq. (16), the reaction rate is therefore thought to decrease with a rise in airflow flux.

(5) The coefficient of the intrinsic reaction rate, k, is thought to increase greatly with a rise in temperature, leading to an increase in the mass transfer rate. According to Eq. (16), the macroscopic reaction rate should also increase, consistent with the findings in Table 7.

5. Conclusions

(1) The aim of the current study was to examine the applicability of using organic acid as a catalyst in the oxidation system during wet flue gas desulfurization. Through screening experiments, peracetic acid was selected.

(2) Using intermittent apparatus, the intrinsic oxidation kinetics of sodium sulfite catalyzed by peracetic acid were subsequently studied. The findings showed that the intrinsic reaction was 1.0 order in peracetic acid, 1.5 order in sulfite and zero order in dissolved oxygen. The activation energy rate was determined as $101.6\,\mathrm{kJ\,mol^{-1}}$.

(3) Using bubbling apparatus, the macroscopic oxidation kinetics of calcium sulfite catalyzed by peracetic acid were also investigated by varying the pH, the concentration of calcium sulfite and peracetic acid, the airflow flux and temperature. A mathematical model was also established to include the effect of the intrinsic reaction, the dissolution of calcium sulfite and diffusion of oxygen.

(4) It was concluded that the macroscopic reaction of calcium sulfite catalyzed by peracetic acid is controlled by the diffusion of oxygen. This finding will be beneficial in designing the oxidation process during wet desulfurization.

Acknowledgements

The present work was supported by The National Basic Research Program (973) of China (No. JK00020) and a Doctor Research Fund from North China Electric Power University.

References

[1] A. Lancia, D. Musmarra, F. Pepe, Uncatalyzed heterogeneous oxidation of calcium bisulfite, Chem. Eng. Sci. 51 (1996) 3889–3896.

[2] Q. Zhong, Study on uncatalyzed calcium sulfite oxidation kinetics, J. Nanjing Univ. Sci. Technol. 24 (2000) 172–176 (in Chinese).

[3] Q. Du, S.H. Wu, Q.Y. Zhu, Non-catalytic oxidation kinetics of calcium sulfite in wet limestone-gypsum FGD process, J. Chem. Ind. Eng. 54 (2003) 1490–1493 (in Chinese).

[4] E. Delplancq, P. Casti, J. Vanderschuren, Kinetics of oxidation of calcium sulphite slurries in aerated stirred tank reactors, Chem. Eng. Res. Des. 70 (1992) 291–295.

[5] Y. Zhao, L.D. Wang, X.M. Wang, Study on the macroscopical uncatalyzed oxidation kinetics of desulfurization residual product-calcium sulfite, Proc. Chin. Soc. Electr. Eng. 25 (2005) 116–120 (in Chinese).

[6] A.S. Abdullah, S.M.J. Zaidi, Kinetics of catalytic oxidation of aqueous sodium sulfite, React. Kinet. Catal. Lett. 64 (1998) 343–349.

[7] A.N. Ermakov, A.P. Purmal, Catalysis of HSO_3^-/SO_3^{2-} oxidation by manganese ions, Kinet. Catal. 43 (2002) 249–260.

[8] K. Hjuler, K.D. Johansen, Wet oxidation of residual product from spray absorption of sulphur dioxide, Chem. Eng. Sci. 49 (1994) 4515–4521.

[9] Q. Du, S.H. Wu, Q.Y. Zhu, Mn-catalyzed oxidation kinetics of calcium sulfite in wet FGD process, J. Harbin Inst. Technol. 36 (2004) 391–394 (in Chinese).

[10] C.H. Barron, H.A. O'Hern, Reaction kinetics of sodium sulfite oxidation by the rapid-mixing method, Chem. Eng. Sci. 21 (1966) 397–404.

[11] W.P. Bronlkowska, T. Bronlkowskl, M. Ulejczyk, Mechanism and kinetics of autoxidation of calcium sulfite slurries, Environ. Sci. Technol. 26 (1992) 1976–1981.

[12] G. Lente, I. Fabian, Kinetics and mechanism of the oxidation of sulfur by iron at metal ion excess, J. Chem. Soc. Dalton. Trans. 5 (2002) 778–784.

[13] M. Vorbach, R. Marr, M. Siebenhofer, Catalytic oxidation of sulfite/bisulfite in a falling-film absorption column, in: Proceedings of the Third International Symposium on Reaction Kinetics and the Development and Operation of Catalytic Processes, Oostende, April 22–25, 2001, p. 575.

[14] G.K. Semler, R. Marr, M. Siebenhofer, Experimental investigation and modeling of catalytically supported sulfite /bisulfite oxidation with oxygen, Chem. Eng. Technol. 27 (2004) 630–633.

[15] Y. Zhao, L.D. Wang, X.M. Wang, Experimental study on effect of inhibitors on macroscopical oxidation kinetics of calcium sulfite, J. Environ. Sci. 17 (2005) 483–487.

[16] Y.Z. Xiang, D.H. Xia, Decreasing olefin content in gasoline by hydrogen peroxide-organic acid, J. Univ. Pet. 29 (2005) 119–121 (in Chinese).

[17] X.Y. Wang, B.Y. Zhao, Y.C. Xie, Spontaneous monolayer dispersion of organic acids on the surface of γ-Al_2O_3 and studies on surface structure of benzoic-γ-Al_2O_3 system, Acta Chim. Sinica 58 (2000) 759–765 (in Chinese).