# Effect of inhibitors on macroscopical oxidation kinetics of calcium sulfite

ZHAO Yi[1], WANG Li-dong[1], WANG Xiao-ming[2], LI Qiang-wei[1], XU Pei-yao[1]

(1. School of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China. E-mail: hgxzy@sina.com;
2. State Power Environmental Protection Research Institute, Nanjing 210031, China)

**Abstract:** In the presence of inhibitors, the macroscopical oxidation kinetics of calcium sulfite, the main byproduct in wet limestone scrubbing, was studied for the first time by adding different inhibitors and varying pH, concentration of calcium sulfite, oxygen partial pressure, concentration of inhibitors and temperature. The mathematical model about the general oxidation reaction was established, which was controlled by three steps involving dissolution of calcium sulfite, mass transfer of oxygen and chemical reaction in the solution. It was concluded that the general reaction was controlled by mass transfer of oxygen under uncatalyzed conditions, while it was controlled by dissolution of calcium sulfite after adding three kinds of inhibitors. Thus, the theory was provided for investigating the mechanism and oxidation kinetics of sulfite. The beneficial references were also supplied for design of oxidation technics in the wet limestone scrubbing.
**Keywords:** calcium sulfite; macroscopical; oxidation; kinetics; inhibitor

## Introduction

Wet limestone scrubbing was the flue gas desulfurization (FGD) process, which had reached the widest diffusion at present. Oxidation was an important chemical course in the desulfurization process, in which the calcium sulfite in the slurry was oxidized into sulfate ( Yan, 1997 ). Since Bäckström proposed a generally accepted chain propagation mechanism, oxidation kinetics of sulfite in the solution had received much attention, which was still uncertain up to now.

The reaction kinetics have two aspects; characteristic kinetics and macroscopical kinetics. The characteristic kinetics was to study the mechanism of chemical reaction under ideal conditions, which was usually carried under homogeneous conditions. While under the industrial conditions, the processes of chemical reaction and mass transfer were carried through at the same time, the integration of which was called macroscopical reaction. Therefore, it was not only to consider the characteristic chemical reaction, but also take the mass transfer of reagents and resultants into account between different phases for research of the macroscopical kinetics, which was usually carried through under heterogeneous conditions ( Zhu, 2004 ). The forced oxidation was adopted in the most wet limestone scrubbing at present. Calcium sulfite in the absorber was oxidized into sulfate by oxygen, which was injected by the oxidation air blower in practice. Thus the research of macroscopical kinetics was much more significant for the practice.

The catalyzed oxidation kinetics of sulfite had been largely studied in the past. It was shown that the reaction rate was greatly enhanced by transition metals, such as manganese and iron(Tatani, 2003; Ermakov, 2002). However, there was little special research reported on the inhibitors, which would have great effect on the oxidation of sulfite. Alcohol, mannitol, and amine were found to reduce the reaction rate, and a considerable reduction, by a factor of 25, was observed with 5% glycerol( Linek, 1981 ). Lancia indicated that the presence, even in traces, of inhibitors, such as alcohol, would strongly affect the reaction rate(Lancia, 1996). Linek and Vacek found that the cuprous ions were produced, which would have a moderate inhibitory effect, during the oxidation process of sulfite catalyzed by cupric ions( Linek, 1981 ). Hjuler indicated that ferrous ions would act as inhibitors in the oxidation of sulfite( Hjuler, 1994 ), although ferric ions acted as catalyzers. Wei found that EDTA, hydroquinone (HQ for abbr.) and pyrocatechol would have inhibitory effect on the oxidation of sulfite ( Wei, 1999 ). However, it was only to simply open out the inhibitory effect of some substances on the oxidation of sulfite in the previously reported work, which was less systematic and theoretical.

There had been no thorough studies on the macroscopical oxidation kinetics of sulfite in presence of inhibitors up to now.

Based on the above results of investigation, wet limestone scrubbing being as background, phenol, alcohol and hydroquinone ( HQ ) were selected as inhibitors, which were in existence in wet limestone scrubbing, such as hydroxybenzene ( Zhao, 2003 ) the macroscopical oxidation kinetics of calcium sulfite in the presence of inhibitors was thoroughly investigated under heterogeneous conditions. Thus the mechanism of macroscopical oxidation kinetics of calcium sulfite was disclosed, which had not been reported in the past.

## 1 Experiment

### 1.1 Experiment apparatus and reagents
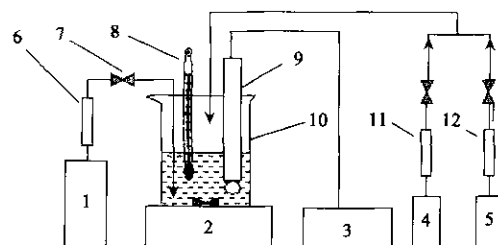
The designed experimental apparatus is shown as Fig.1.



Fig.1 Sketch of the experimental apparatus for oxidation of calcium sulfite in the presence of inhibitors
1. YL90S-2 air compressor; 2. 79HW-1 magnetic constant temperature stirrer; 3. pHS-2C pH meter; 4. hydrochloric solution in concentration of 1:3; 5. ammonia solution in concentration of 1:3; 6. LZB glass rotameter for gas; 7. valve; 8. thermometer; 9. combined pH electrode; 10. reactor(beaker of 250 milliliter); 11,12. LZB glass rotameter for liquid

Reagents: Calcium sulfite, hydrochloride acid, ammonia, barium chloride, phenol ( concentration of 6.07% ), alcohol, HQ, EDTA, all were analytical purity reagent;

Fixing reagent: The solution with 75 g NaCl, 300 ml of distil water, 30 ml of HCl, 50 ml of glycerol and 100 ml of alcohol was blended equably;

Standard solution of sulfate: The solution with 1.4787 g of anhydrous sodium sulfate was diluted to 1000 ml by distilled water.

### 1.2 Experimental measures

### 1.2.1 Analytical measure

The concentration of sulfate was measured by turbidimetric method ( Sanitary Institute of Chinese Medical Academy, 1972 ). The observed oxidation rate would be calculated by the equation(Zhong, 2000):

$$R = \frac{C_t - C_0}{t}. \qquad (1)$$

### 1.2.2 Oxidation experiments of calcium sulfite in the presence of inhibitors

150 ml of distill water was added into the reactor when the temperature, rotation speed of stirrer and velocity of airflow were adjusted to the fixed values. Air was injected into the reactor when some known quantity of inhibitors and calcium sulfite were added into the water. Solution of hydrochloric and ammonia were used to adjust the pH. The temperature, velocity of airflow and pH should be observed and adjusted to the set value during the course of reaction. The production was dissolved by hydrochloric acid at the fixed time. The concentration of sulfate was measured and the initialization involved in the sulfite was taken out.

## 2 Results and discussion

### 2.1 Comparison of the inhibitory effect about several kinds of inhibitors

Effects of the inhibitors were compared with each other by carring out the oxidation experiments of calcium sulfite in the presence of EDTA, phenol, alcohol and HQ respectively. According to Section 1.2.2, after 1 g of calcium sulfite was added into 150 ml of distil water, 0.23 g of EDTA, 1 ml of alcohol, 5 ml of phenol solution and 0.5 g of HQ, were added respectively. The temperature was kept at 30℃, the velocity of airflow was kept at 0.056 $m^3/h$ and pH was kept at 6.0. Oxidation lasted 30 min and the results are shown in Fig.2.
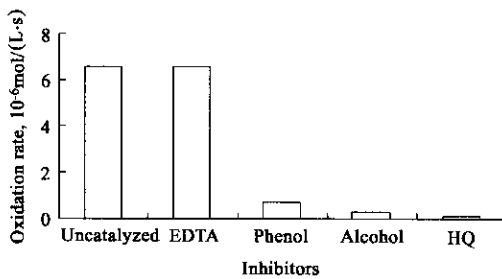


Fig.2 Inhibitory effect of the different inhibitors
Calcium sulfite, 1 g; distil water, 150 ml; EDTA, 0.23 g or alcohols, 1 ml or phenols solution, 5 ml or hydroquinone, 0.5 g; velocity of airflow, 0.056 $m^3/h$; temperature, 30℃; pH 6.0; oxidation time, 30 min

It is shown that EDTA had no effect on the oxidation rate, which was different from Wei's result(Wei, 1999). It was obvious that the oxidation rate would be greatly inhibited by phenol, alcohol and HQ. Therefore, phenol, alcohol and HQ were selected as significant substances to study the macroscopical oxidation kinetics of calcium sulfite in presence of inhibitors.

### 2.2 Effect of pH on inhibition

According to Section 1.2.2, after 1 g of calcium sulfite was added into distil water, inhibitors(1 ml of alcohol, 5 ml of phenol solution and 0.5 g of HQ)were added respectively. The temperature was kept at 30℃ and the velocity of airflow was kept at 0.056 $m^3/h$. Oxidation lasted 30 min under different pH conditions. Effect of pH on the inhibition is shown in Fig.3.

It is shown in Fig.3 that uncatalyzed oxidation rate of calcium sulfite would decrease with the increase of pH, but the effect of pH was not significant. The tendency would not change after adding the three kinds of inhibitors. The inhibitory effect of phenol would be weakened evidently with the decrease of pH, while it was not evident with regard to alcohol and HQ.

### 2.3 Effect of concentration of calcium sulfite on inhibition
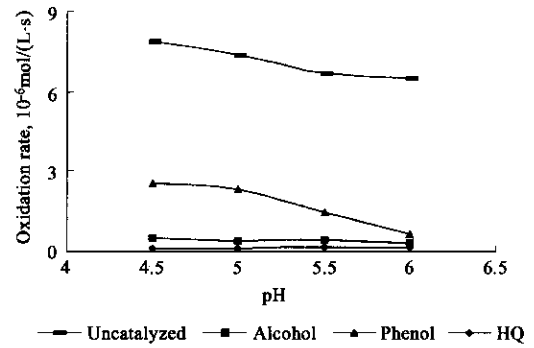
Under the other same conditions in Section 2.2, pH was



Fig.3 Effect of pH on the inhibition
Calcium sulfite 1 g; distil water 150 ml; alcohols(1 ml) or phenols solution(5 ml) or hydroquinone(0.5 g); velocity of airflow 0.056 $m^3/h$; temperature 30℃; oxidation time 30 min

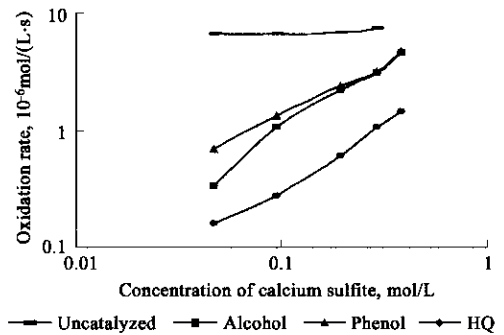kept at 6.0. With different concentrations of calcium sulfite, its effect on the inhibition is shown in Fig.4.



Fig.4 Effect of concentration of calcium sulfite on the inhibition
Distil water 150 ml; alcohols(1 ml) or phenols solution(5 ml) or hydroquinone (0.5 g); velocity of airflow 0.056 $m^3/h$; temperature 30℃; pH 6.0; oxidation time 30 min

It can be seen in Fig.4 that uncatalyzed oxidation rate was zero order in calcium sulfite, which was consistent with the results from Hjuler *et al*. (Hjuler, 1994). After adding three kinds of inhibitors, the oxidation rate would increase with the increase of concentration of calcium sulfite, which was approximately 1.0 order in sulfite.

### 2.4 Effect of oxygen partial pressure on inhibition

With the same conditions in Section 2.2, pH was kept at 6.0. The effect of velocity of airflow on the inhibition is shown in Fig.5. As velocity of airflow was in proportion to oxygen partial pressure at the same time, the effect of oxygen partial pressure on inhibition is equally shown in Fig.5.
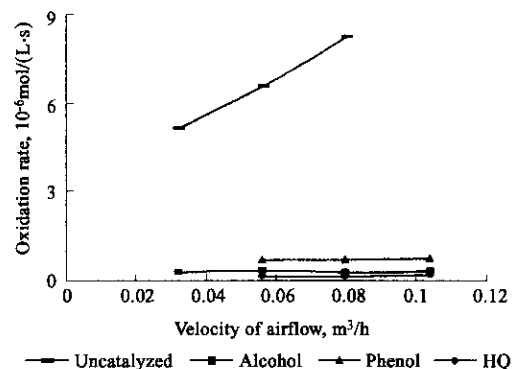


Fig.5 Effect of oxygen partial pressure on the inhibition
Calcium sulfite 1 g; distil water 150 ml; alcohols(1 ml) or phenols solution(5 ml) or hydroquinone(0.5 g); temperature 30℃; pH 6.0; oxidation time 30 min

Fig.5 shows that uncatalyzed oxidation rate was 0.5 order in the oxygen partial pressure. After adding three kinds

of inhibitors, oxidation rate would turn to zero order oxygen partial pressure.

## 2.5 Effect of concentration of inhibitors on inhibition

Under the same conditions shown in Section 2.2, pH was kept to 6.0. With different concentrations of inhibitors, its effect on the inhibition is shown in Fig.6.
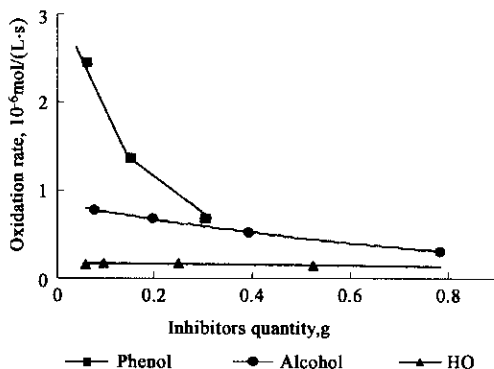


Fig.6 Effect of concentration of inhibitors on the inhibition
Calcium sulfite 1 g; distil water 150 ml; velocity of airflow 0.056 m³/h; temperature 30 ℃; pH 6.0; oxidation time 30 min

It indicates in Fig.6 that oxidation rate would decrease with the increase of concentration of alcohol and phenol. The inhibitory effect would increase evidently with the increase of its concentration for phenol, while it was not evident for alcohol. And the concentration of HQ had no effect on its inhibiting effect in the experimental concentration scope, which indicated it would have effect at low concentration. It was obvious that the oxidation rate of calcium sulfite decreased in the following order: inhibited by phenol, by alcohol and by HQ, which was especially evident in low concentration scope of inhibitors. It also shows that the inhibitory effect of alcohol and HQ was stronger than phenol, which was consistent with that in Section 2.1.

## 2.6 Effect of temperature on inhibition

Under the other same conditions in Section 2.2, pH was kept to 6.0. With different temperature, its effect on the inhibition is shown in Fig.7.
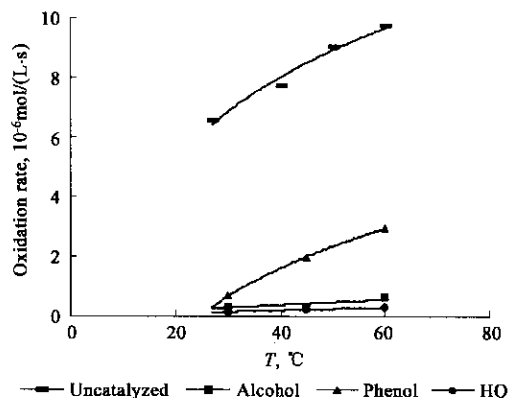


Fig.7 Effect of temperature on the inhibition
Calcium sulfite 1 g; distil water 150 ml; alcohols(1 ml) or phenols solution(5 ml) or hydroquinone(0.5 g); velocity of airflow, 0.056 m³/h; pH 6.0; oxidation time 30 min

It is shown in Fig. 7 that the oxidation rate would increase with the increase of temperature in all the experiments, which was evident while uncatalyzed or inhibitoried by phenol and unobvious while inhibitoried by alcohol or HQ. It indicates that increase of temperature, which was helpful for oxidation of sulfite, would lower the inhibitory effect of phenol. However, the inhibitory effect of alcohol and HQ was insensitive to temperature, which indicated their inhibitory effect was stronger than phenol.

## 2.7 Mechanism of macroscopical oxidation kinetics of calcium sulfite

In wet limestone scrubbing, solid of calcium sulfite dissolved into liquid phase and reacted uncatalyzed with dissolved oxygen, which was injected by oxidation air blower and transferred from gas phase into liquid phase.

$$HSO_3^-, SO_3^{2-} + \frac{1}{2}O_2 \rightarrow HSO_4^-, \quad SO_4^{2-}. \quad (2)$$
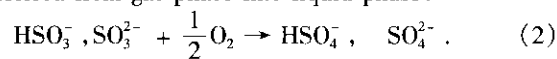
The above reaction was an expression according to the molar ratio, instead of elementary reaction. The oxidation kinetics would be achieved only by experiments. The oxidation process of calcium sulfite could be divided into three steps under heterogeneous conditions, which included dissolution of calcium sulfite whose rate was $R_A$ from the solid particles to the liquid, mass transfer of oxygen into the liquid whose rate was $R_B$ and the chemical reaction whose rate was $R_C$ in the liquid phase.

### 2.7.1 Dissolution rate $R_A$ of calcium sulfite

The samples of calcium sulfite were supposed to be the same sized small balls in the amount of $N$, whose radius was $r_j$. The solute would transfer from the surface of balls into solution, whose bulk was $V$. According to Fick's law(Chen, 2004), the transfer rate was $\left( -4\pi r^2 D \dfrac{\partial C}{\partial r} \right)$. It could be derived from balance of materials:

$$V \cdot \frac{\partial C}{\partial t} = -4\pi r^2 \cdot D \cdot N \cdot \frac{\partial C}{\partial r}, \quad (3)$$
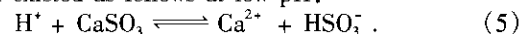
boundary conditions:

$$C = C_S \quad \text{while } r = r_j;$$
$$C = C_B \quad \text{while } r = +\infty.$$

It was inferred as follows:

$$R_A = \frac{\partial C}{\partial t} = \frac{4\pi D r_j \cdot N}{V}(C_S - C_B). \quad (4)$$

The reaction existed as follows at low pH:

$$H^+ + CaSO_3 \rightleftharpoons Ca^{2+} + HSO_3^-. \quad (5)$$

Thus $D$ was increased and (4) was modified

$$R_A = \frac{4\pi D r_j \cdot N \cdot \varepsilon}{V}(C_S - C_B). \quad (6)$$

### 2.7.2 Mass transfer rate $R_B$ of oxygen

For the irreversible Reaction (2), kinetics equation about the characteristic reaction was given:

$$R_B = k[O_2]^m[SO_3^{2-}]^n. \quad (7)$$

The diffusion and chemical reaction were simultaneous while oxygen was absorbed into the liquid. Thus the sub-coefficient was increased and the mass transfer coefficient was changed accordingly. The mass transfer rate of oxygen was given according to theory of double film

$$R_B = k_L'(C_{Ai} - C_A) = k_L\alpha(C_{Ai} - C_A), \quad (8)$$

$$\alpha = \frac{a}{tha}, \quad (9)$$

where $a$ was fit by the relation

$$a = L\sqrt{\left(1 - \frac{\alpha - 1}{U}\right)^n},$$

where $L$ and $U$ were decided(Hao, 1990) by

$$L = \frac{1}{k_L}\sqrt{\frac{2}{m+1}D_A kC_{Ai}^{m-1} C_B^n},$$

$$U = \frac{C_B}{2C_{Ai}} \cdot \frac{D_B}{D_A}.$$

As the chemical reaction was rapid, it was simplified by considering $\alpha \approx L$

$$k_L' = \alpha \cdot k_L \approx Lk_L = \sqrt{\frac{2}{m+1}D_A kC_{Ai}^{m-1} C_B^n}, \quad (10)$$

$$R_B = k_L'(C_{Ai} - C_A)$$

$$= \sqrt{\frac{2}{m+1}D_A kC_{Ai}^{m-1} C_B^n} \cdot (C_{Ai} - C_A). \quad (11)$$

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

$$R_B = \sqrt{\frac{2}{m+1} D_A k C_{Ai}^{m-1} C_B^n} \cdot C_{Ai}$$

$$= \sqrt{\frac{2}{m+1} D_A k C_{Ai}^{m+1} C_B^n}$$

$$= \sqrt{\frac{2}{m+1} D_A k \left(\frac{P}{m_{pc}}\right)^{m+1} C_B^n} . \qquad (12)$$

It was inferred from Equation (12) that the mass transfer rate was 0.5 order in oxygen partial pressure while the chemical reaction rate was zero order in dissolved oxygen.

### 2.7.3 Chemical reaction rate $R_C$

For the characteristic oxidation reaction of sulfite, it was inferred from the chain reaction mechanism proposed by Bronlkowska proved by Barron(Barron, 1966; Bronlkowska, 1992):

$$R_C = k C_M^{1/2} C_{S(IV)}^{3/2} . \qquad (13)$$

It was shown that the chemical reaction rate was zero order in dissolved oxygen and 3/2 order in sulfite.

### 2.7.4 General reaction rate $R$

As the three above steps proceed simultaneously, the general reaction rate depended on the slowest step

$$R = \min(R_A, R_B, R_C) . \qquad (14)$$

The characteristics of uncatalyzed oxidation of calcium sulfite in the experimental system were as follows:

(1) It is shown in Fig.5 that uncatalyzed oxidation rate was 0.5 order in the oxygen partial pressure, which showed $R = R_B$. As calcium sulfite was saturated in the reaction solution and concentration of sulfite ion could be regarded as constant, the general reaction rate was 0 order in calcium sulfite, which was consistent with Fig.4. It was inferred that the general reaction was controlled by mass transfer of oxygen.

(2) With the decrease of pH, the dissolution rate increased which would lead to the increase of sulfite ion. According to Equation (12), the mass transfer rate of oxygen would increase as well as the general reaction rate, which was consistent with Fig.3.

(3) The chemical reaction rate $R_C$ increased which would lead to the increase of $k$ in Equation (12) while the temperature increased. The general reaction would increase accordingly, which was consistent with Fig.7.

Inhibitors would have effect on the oxidation of calcium sulfite in the following way:

Inhibitors could react with catalyst, such as cobalt and manganese, and restrained their catalysis by forming steady compound. For example, EDTA would inhibitor the oxidation of calcium sulfite by forming chelate complex in the manganese catalyzing system. If EDTA was added into uncatalyzed oxidation system of calcium sulfite, it would have no effect on the oxidation rate. The reaction was as follows:

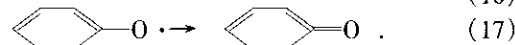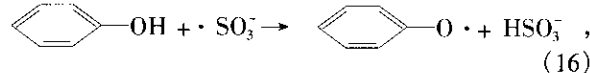$$Na_2 EDTA + Mn^{2+} \longrightarrow MnEDTA + 2Na^+ . \qquad (15)$$
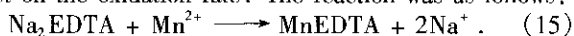
As calcium sulfite used in the experiments was analytical purity reagent in which there was no catalyst impurity such as transition metals, EDTA had no effect on reaction rate, which is consistent with Fig.2.

Inhibitors could have effect on the oxidation rate by reducibility. For example, as a kind of effective reductant, HQ competed for the dissolved oxygen with sulfite, which would inhibit the oxidation. It is shown in Fig.6 that there were about $1.74 \times 10^{-3}$ mol of sulfite oxidized during the 30 min uncatalyzed reaction. That was to say, there was at least $8.7 \times 10^{-4}$ mol of oxygen dissolving and reacting as oxidant. When about 0.06 g of HQ was added under the condition, $4.4 \times 10^{-5}$ mol of sulfite oxidized. Supposing HQ inhibited the oxidation by competing for dissolved oxygen, there should be $8.5 \times 10^{-4}$ mol of oxygen reacting with HQ which was
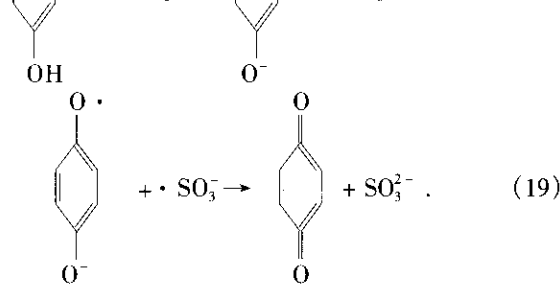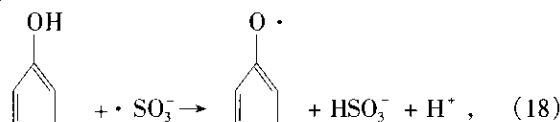
much more than what could react. Therefore, reducibility of HQ was not the primary factor that inhibited the oxidation in the experimental system. It was the same with alcohol, phenol.

As the chain terminator, inhibitors could inhibit the oxidation by eliminating the free radicals produced in the process of reaction. For example, alcohol reacted with $\cdot SO_3^-$ which would terminate the chain reaction. There were many inhibitors such as HQ, phenol, alcohol and glycerol, which had active hydroxide radicals and reducibility. The reactions were as follows.
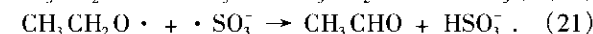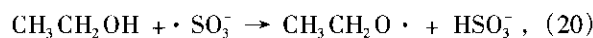
( I ) Phenol

$$(16)$$
$$(17)$$

( II ) HQ

$$(18)$$
$$(19)$$

( III ) Alcohol

$$CH_3CH_2OH + \cdot SO_3^- \rightarrow CH_3CH_2O \cdot + HSO_3^- , \qquad (20)$$
$$CH_3CH_2O \cdot + \cdot SO_3^- \rightarrow CH_3CHO + HSO_3^- . \qquad (21)$$

Uncatalyzed oxidation kinetics of calcium sulfite under heterogeneous condition was changed after adding to the three above inhibitors and the characteristics were given.

(4) Free radicals $\cdot SO_3^-$ were mostly absorbed and chemical reaction rate $R_C$ decreased greatly. Equation (13) was not applicable any longer. As there was little sulfite consumed by chemical reaction in unit time, the solution was approximately saturated. The dissolution rate was proportional to amount of the small balls, which was also to the quantity of calcium sulfite. Thus, the general reaction rate, controlled by dissolution of sulfite, was 1.0 order in calcium sulfite from the macroscopical angle, which was consistent with Fig. 4.

(5) Mass transfer rate of oxygen $R_B$ decreased and was much greater than chemical reaction rate. The chemical reaction had little effect on oxygen absorbing which was approximate physical absorbing process. As the rate of oxygen consumed by chemical reaction was rather little, oxygen in the solution was saturated during the reaction. Thus the concentration of oxygen was regarded as constant and the general reaction was zero order in oxygen partial pressure, which was consistent with Fig.5.

(6) The more inhibitors added, the lower chemical reaction rate would be, which would lead to the less sulfite consumed in unit time and the more saturated of solution. The dissolution rate of a single ball would decrease accordingly. When the inhibitors were excessive, chemical reaction rate would decrease to a critical value. Thus the dissolution rate of ball would not decrease and the general reaction nearly ceased, which was consistent with Fig.6.

(7) When pH decreased, mass transfer coefficient $D$ would increase and the general reaction rate would increase, which was consistent with Fig.3.

(8) The chemical reaction rate would increase when the temperature increased. But the general reaction rate would not increase greatly because of the effect of inhibitors. The stronger inhibitory effect being, the phenomena would be more evident, which could be seen from that of alcohol and HQ in Fig.7.

## 3    Conclusions

Wet limestone scrubbing being as background, the macroscopical oxidation kinetics of calcium sulfite in presence of inhibitors was experimentally investigated for the first time. The mathematical model about the general oxidation reaction, which was controlled by three steps involving dissolution of calcium sulfite, mass transfer of oxygen and chemical reaction in the solution, was established.

In the experimental system, uncatalyzed oxidation rate was zero order in concentration of calcium sulfite and 0.5 order in oxygen partial pressure. The macroscopical kinetics would change after adding the inhibitors and the oxidation rate was 1.0 order in concentration of calcium sulfite and zero order in oxygen partial pressure. Integrated with the mathematical model, it was inferred that the general reaction controlled by mass transfer of oxygen under uncatalyzed conditions, while by dissolution of sulfite after adding the inhibitors.

By analyzing the mechanism of inhibited reaction, it was inferred that uncatalyzed oxidation was free chain reaction and the free radicals, which were only a little, could be produced without transition metals and UV in the experiments. Inhibitors, such as alcohol, phenol and HQ, could have effect on the reaction by eliminating the free radicals, which was different from the inhibitory mechanism of EDTA. These kinds of inhibitors, which had active hydroxide radicals and reducibility, might also include glycerol, tea polyphenols, ascorbic acid and other substances.

Thus, the theory was provided for investigating the mechanism and oxidation kinetics of sulfite. The beneficial references were also supplied for design of oxidation technics in the wet limestone scrubbing.

### Notation:

$\alpha$ is the enhancing coefficient in liquid phase $= \dfrac{k'_L}{k_L}$; $C_A$ is the concentration of oxygen in the solution; $C_{Ai}$ is the equilibrium concentration of oxygen at the interface; $C_B$ is the concentration of calcium sulfite particles; $C_M$ is the concentration of catalyst; $C_S$ is the saturation concentration of calcium sulfite particles; $C_{S(IV)}$ is the concentration of sulfite ion; $C_t$ is the concentration of calcium sulfate after reaction

(mol/L); $C_0$ is the initial concentration of calcium sulfate (mol/L); $D$ is the mass transfer coefficient of calcium sulfite particles; $D_A$ is the mass transfer coefficient of A in the liquid phase; $D_B$ is the mass transfer coefficient of B in the liquid phase; $L$ is the ratio of chemical reaction rate in the liquid film to diffusion rate through the liquid film about A in the double film model; $m$ is the chemical reaction order in dissolved oxygen; $m_{PC}$ is the equilibrium constant at the interface; $N$ is the amount of calcium sulfite particles whose diameter was $r_j$ in unit of solution; $n$ is the chemical reaction order in sulfite; $P$ is the oxygen partial pressure in gas phase; $t$ is the reaction time(s); $U$ is the ratio of diffusion rate about B(sulfite) to that about A through the liquid film; $V$ is the bulk of the solution; $\varepsilon$ is the enhancing coefficient.

## References:

Barron C H, O'Hern H A, 1966. Reaction kinetics of sodium sulfite oxidation by the rapid-mixing method[J]. Chemical Engineering Science, 21: 397—404.

Bronlkowska W P, Bronlkowskl T, Ulejczyk M, 1992. Mechanism and kinetics of autoxidation of calcium sulfite slurries [J]. Environmental Science Technology, 26: 1976—1981.

Chen J N, 2004. Mechanism of transfer course[M], Beijing: Chemical Industry Publishing House. 252—261.

Ermakov A N, Purmal A P, 2002. Catalysis of $HSO_3^-$ /$SO_3^{2-}$ oxidation by manganese ions[J]. Kinetics and Catalysis, 43(2): 249—260.

Hao J M, Ma G D, 1990. Controlling engineering of air pollution[M]. Beijing: Higher Education Publishing House. 303—305.

Hjuler K, Johansen K D, 1994. Wet oxidation of residual product from spray absorption of sulphur dioxide[J]. Chemical Engineering Science, 49(24A): 4515—4521.

Lancia A, Musmarra D, Pepe F, 1996. Uncatalyzed heteroeneous oxidation of calcium bisulfite[J]. Chemical Engineering Science, 51(16): 3889—3896.

Linek V, Vacek V, 1981. Chemical engineering use of catalyzed sulfite oxidation kinetics for the determination of mass transfer characteristics of gas-liquid contactors[J]. Chemical Engineering Science, 36(11): 1747—1768.

Sanitary Institute of Chinese Medical Academy, 1972. Method of water quality analysis[M]. Beijing: Demotic Sanitary Publishing House. 90—92.

Tatani A, Imai T, Fujima Y et al., 2003. Crystallization of calcium sulfite and behavior of $Mn^{2+}$ [J]. Journal of Chemical Engineering of Japan, 36(9): 1057—1062.

Wei G, Xiong R C, Zhang X D et al., 1999. Inhibition of some materials on sulfite oxidation[J]. Technology of Water Treatment, 25(5): 277—280.

Xiong R C, Wei G, Zhang X D, 1999. Inhibition of hydroquinone on sulfite oxidation[J]. Journal of Beijing University of Chemical Technology, 26(1): 68—71.

Yan J, 1997. Controlling oxidation in wet desulfurization [J]. Electric Environment Protection, 13(2): 41—44.

Zhao Y, 2003. Evaluation of environment quality[M]. Beijing: Chinese Electric Power Publishing House. 157.

Zhong Q, 2000. Study on uncatalyzed calcium sulfite oxidation kinetics [J]. Nanjing University of Science and Technology Transaction, 24(2): 172—176.

Zhu B C, 2004. Chemical reaction engineering[M], Beijing: Chemical Industry Publishing House. 1—7.