The Oxidation Kinetics of Magnesium Sulfite in Homogenous System

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ABSTRACT: The oxidation rate of magnesium sulfite is important for the application of wet magnesia desulfurization, which is suitable for the industrial boilers in china. In this work, the oxidation rate of magnesium sulfite without addition in homogeneous condition is studied, magnesium sulfite was oxidated in the bath and temperature constant reactor with injecting nitrogen into the upper space to remove air. With adding different concentration of magnesium sulfite, the sulfite oxidation rate was found to be 1.15th order in sulfite concentration, and the dissolved oxygen was 0.30th order to the sulfite oxidation rate, the oxidation rate in different temperature was also discussed, and the activation energy was found to be 87.36 kJ/mol. Based on the experiment results, a simple model of the magnesium sulfite oxidation kinetics was built.
KEYWORD: Magnesium desulfurization; Sulfite; Homogeneous; Oxidation rate

1 INTRODUCTION

Wet flue gas desulfurization (WFGD) is widely used in power plants in China at present, and limestone-gypsum desulfurization is the most popular, but there are still about 500,000 units of industrial boilers without flue gas desulfurization which discharge 7,000,000 tons of SO_2 to the atmosphere per year, Xin (2010) also indicated the industrial boilers had become the second emission source of SO_2. The technology of limestone-gypsum desulfurization is more complicated and expensive, so magnesia desulfurization which has lower operating cost and higher recovery efficiency of by-product is more suitable than limestone-gypsum desulfurization for industrial boilers.

Magnesia desulfurization byproduct is mainly composed of magnesium sulfite and magnesium sulfate, so there could be two recovery approaches in terms of the byproduct, including recycle of magnesia by regeneration and recovery of magnesium sulfate by oxidation. The specific value of magnesium sulfate or magnesium sulfite is determined by the oxidation of sulfite in FGD process. So the mechanism of the oxidation of magnesium sulfite is important for the application of the magnesia desulfurization.

The oxidation of sodium sulfite and calcium sulfite has been investigated for several years, especially the influence of metal ions(Co^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+})catalysts were discussed in the studies of Wanda(1992), both Wilkinson(1993) and Ermakov (2002) did many researches of sulfite oxidation in heterogeneous condition. The research of Lancia (1996) and Lewis (2005) indicated that the investigation of sulfite oxidation was mainly about calcium sulfite and sodium sulfite, studies of magnesium sulfite oxidation is not common.

Wang (2010) studied both of intrinsic and macroscopic kinetics, which is carried out in homogeneous conditions and heterogeneous conditions respectively. The oxidation kinetics in homogeneous is studied the mechanism of oxidation, which is important for revealing behavior of the oxidation reaction. But macroscopic reaction was investigated more, because of the similar reaction condition with the desulfurization process and the remarkable practical significance.

Zhong (2000) had researched the kinetics of calcium sulfite oxidation in heterogeneous condition, and the reaction rate was found to be 1st order in oxygen and 0th or 0.75th in sulfite concentration, respectively. His study also discussed the influence of pH and the addition of Mn^{2+}. Wang (2009) had found the macroscopic oxidation in heterogeneous should be controlled by the intrinsic reaction rate.

The aim of this work is to study the mechanism of magnesium sulfite oxidation in homogeneous obtained by contacting sulfite with the oxygen saturated solution.

2 EXPERIMENTS

2.1 *Facility and process*

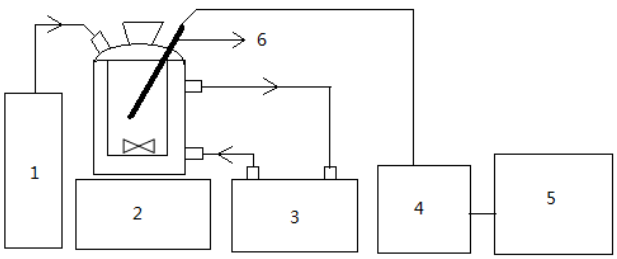
A bath reactor is shown in Figure 1, When 600 ml de-ionized oxygen saturated water was added, the pure nitrogen was delivered to the above of water into the reactor for avoiding the interference of the other gas(such as air or oxygen) at the same time. The temperature of the reactor was kept constant by the flowing water in the interlayer from the constant temperature water-bathing. The dissolved oxygen sensor in the water was monitoring the concentration of the dissolved oxygen. When the oxygen saturated water was constant to the appointed temperature, the magnesium sulfite with known concentration was supplied into the reactor. Then oxidation reaction was started, the computer recorded the change of dissolved oxygen concentration.

2.2 *Reaction model*

The overall oxidation reaction stoichiometry corresponds to the equation

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

According to the equation, the whole reaction rate R was determined by 3 kinds of rate: R=f (r_1+r_2+r_3) , r_1 is the dissolved rate of sulfite, sometimes also includes the sulfite diffusion rate caused by the concentration uneven distribution, r_2 is the mass transfer rate of oxygen, r_3 is the rate of intrinsic reaction.



1-nitrogen, 2-magnetic stirrer,3-temperature constant water-bathing, 4-dissolved oxygen monitor, 5-computer, 6-dissolved oxygen sensor

Figure 1. Homogeneous oxidation reaction facility

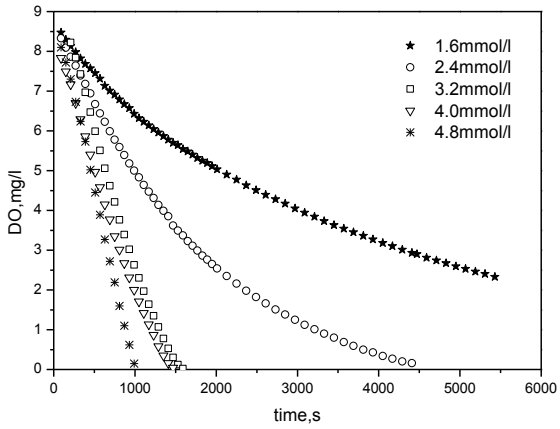


Figure 2. Dissolved oxidation with different sulfite concentration at 298K

In homogeneous condition, the intrinsic oxidation was influenced by the concentration of sulfite (c_s), the dissolved oxygen (c_o), and the temperature (T) of the reaction solution.

On the basis of the reaction kinetics, the homogeneous oxidation rate r:

$$r = kc_S^a c_O^b \tag{2}$$

And k is reaction rate constant, which just changes with temperature, a is the order of sulfite concentration to the oxidation reaction rate, b is the order of dissolved oxygen concentration to the reaction rate. This equation also can be converted to

$$\lg r = \lg k + a \lg c_S + b \lg c_O \tag{3}$$

The curve in Figure 2 indicated that the concentration of dissolved oxygen was decreasing with time. So the decreasing rate of dissolved oxygen could be taken as the oxidation rate.

$$r = \frac{dc_O}{dT} \tag{4}$$

The equation (2) shows that r is relative with k, so equation (4) is applied to one certain constant temperature.

The Figure 2 also reflected that the concentration of sulfite affected the rate of oxidation quietly.

3 RESULTS AND DISCUSSION

3.1 *The influence of dissolved oxygen at 298K*

Figure 2 showed the relation of dissolved oxygen absorption with the concentration of magnesium sulfite, the curve of 3.2mmol/l sulfite was found to be similar with the curve of 4.0mmol/l, which indicated that the concentration of sulfite would affect the rate of the oxidation during the whole reaction stages, because the dissolved oxygen was

always decreasing, and also indicated there might be an optimal sulfite concentration.

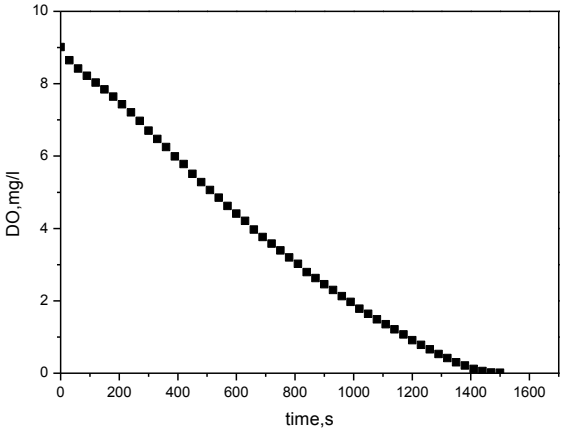


Figure 3. Dissolved oxygen with 3.2mmol/l sulfite at 293K

Figure 3 showed the variation tendency of dissolved oxygen, the reaction solution was oxygen saturated at the beginning, and the reaction was separated into two stages. At the first stage, the curve of dissolved oxygen decreasing was flat, then the curve was steep with the reaction.

From the equation (4), the reaction rate r at 293K can be calculated with figure 3, and 3.2mmol/l sulfite is far more than the need of the reaction, so the sulfite concentration c_S would not be considered in equation (2), then equation (2) can be converted to

$$\lg r = \lg k + b \lg c_O \tag{5}$$

According to the relation of r and c showed in Equation (5), the rate of magnesium sulfite oxidation was found to be 0.30th in dissolved oxygen from figure 4.

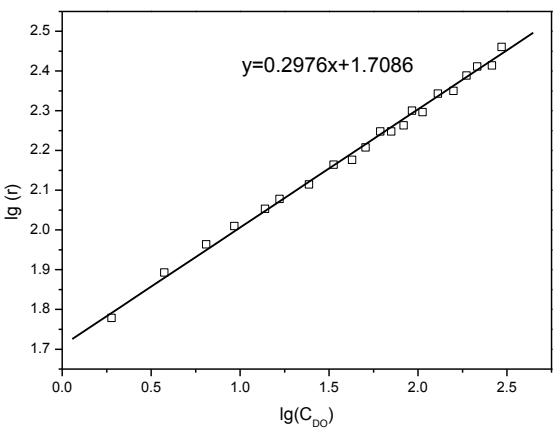


Figure 4. The order of dissolved oxygen

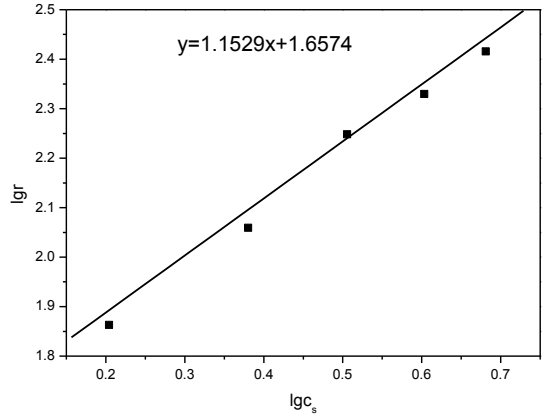


Figure 5. The order of sulfite concentration

3.2 *The influence of sulfite concentration at 298K*

Figure 1 had showed the influence of sulfite concentration to the oxidation, the time of the reaction was becoming less with the increasing of the concentration of sulfite, so the concentration of sulfite would definitely impact the rate of oxidation. But at the beginning of the oxidation, dissolved oxygen concentration was almost the same saturated concentration, which was considered to be unaffected to the reaction rate at this special period, then equation (2) was converted to

$$\lg r = \lg k + a \lg c_S \tag{6}$$

Figure 5 showed that *a* was 1.15, so the rate of sulfite oxidation was found to be 1.15th order in sulfite concentration.

3.3 *The influence of temperature*

Figure 6 indicated the decreasing of dissolved oxygen with time at 293K, 298K, 303K, 308K and 313K separately, the increasing of the temperature had made the rise of oxidation rate.

The temperature could affect the reaction rate constant *k* showed in the equation (2), so *k* is quiet an important parameter to kinetics of the homogeneous oxidation. Theoretically if the temperature increase 10 units, the rate of reaction would increase 2 or 3 times.

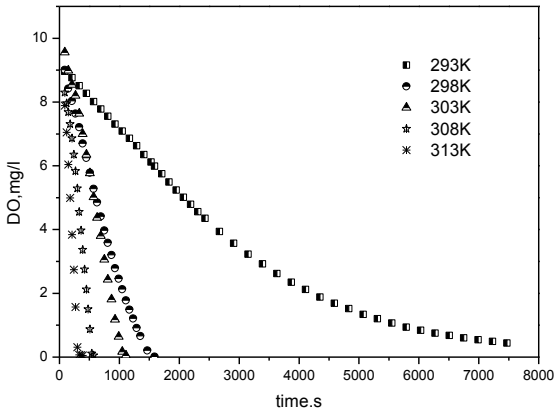


Figure 6. influence of temperature with 3.2mmol/l sulfite

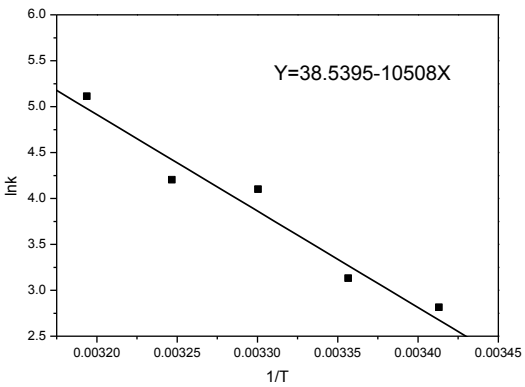


Figure 7. The activation energy of the sulfite oxidation

Using equation (3), k at this five different temperature can be calculated. According to Arrhenius equation $k=k_0e^{-E/RT}$, activation energy can be calculated by

$$\ln k = \ln k_0 - \frac{E}{R}\frac{1}{T} \tag{7}$$

Where k_0 is the coefficient of reaction rate.

The result in Figure 7 indicated activation energy E was 87.36 kJ/mol, which could affect the possibility and difficulty of the oxidation reaction. The activation energy of magnesium sulfite oxidation was big enough for the further research, and the result corresponded to the research of Wang(2013).

4 CONCLUSION

The research on the magnesium sulfite oxidation reaction under the homogeneous condition shows that all of the concentration of dissolved oxygen, the concentration of sulfite and the temperature of the solution could affect the rate of homogeneous oxidation rate, which is consistent with the reaction kinetics equation $r=kc_s^a c_o^b$, and in the result a was to be 0.30 th, b was to be 1.15 th, the activation energy was 87.36 kJ/mol, so the kinetics equation of magnesium sulfite oxidation is $r=kc_s^{1.15}c_o^{0.3}$.

The oxidation rate orders to the dissolved oxygen with different sulfite concentration were found to be similar, so the assumption that the concentration of sulfite was enough for the dissolved oxygen was correct, so do the assumption that the dissolved oxygen would not affect the oxidation rate in the initial stage.

The curve of the dissolved oxygen absorption with 2.4mmol/l and 3.2mmol/l sulfite addition was quite similar, so there might be an optimal initial concentration of sulfite for the absorption of dissolved oxygen, because the concentration of dissolved oxygen was decreasing during the reaction.

Some part of the mechanism of magnesium sulfite oxidation was studied, and there are still amount of work need to do, and magnesia desulfurization can be applied wildly.

ACKNOWLEDGEMENTS

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