

Catalytic oxidation of calcium sulfite in solution/aqueous slurry

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Abstract: Forced oxidation of calcium sulfite aqueous slurry is a key step for the calcium-based flue gas desulfurization (FGD) residue. Experiments were conducted in a semi-batch system and a continuous flow system on lab scales. The main reactor in semi-batch system is a 1000 ml volume flask. It has five necks for continuous feeding of gas and a batch of calcium sulfite solution/aqueous slurry. In continuous flow system, the main part is a jacketed Pyrex glass reactor in which gas and solution/aqueous slurry are fed continuously. Calcium sulfite oxidation is a series of complex free-radical reactions. According to experimental results and literature data, the reactions are influenced significantly by manganese as catalyst. At low concentration of manganese and calcium sulfite, the reaction rate is dependent on 1.5 order of sulfite concentration, 0.5 order of manganese concentration, and zero order of oxygen concentration in which the oxidation is controlled by chemical kinetics. With concentrations of calcium sulfite and manganese increasing, the reactions are independent gradually on the constituents in solution but are impacted by oxygen concentration. Manganese can accelerate the free-radical reactions, and then enhances the mass transfer of oxygen from gas to liquid. The critical concentration of calcium sulfite is 0.007 mol/L, manganese is 10^{-4} mol/L, and oxygen is of 0.2–0.4 atm.

Keywords: calcium-based FGD; calcium sulfite; manganese; catalyzed oxidation

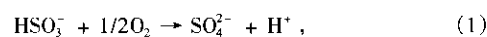
Introduction

Calcium-based FGD process is the most common commercial method for removal of SO_2 emission from combustion of fossil fuel. Scrubbing slurries formed in the process consist of calcium sulfite and sulfate. The slurries presently deposited in environment will bring serious waste problem. So practice use of the slurries becomes a topic of great interest in the study of calcium-based FGD process. Moreover, calcium sulfate is a neutral product, and is usually utilized in the building industry as gypsum. Therefore, the slurries are preferred to calcium sulfate as an end product, and the simplest method for the slurries changed into calcium sulfate is forced oxidation by air.

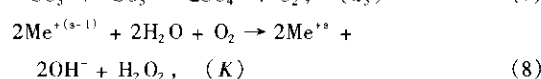
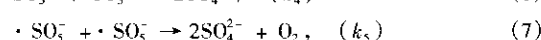
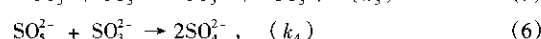
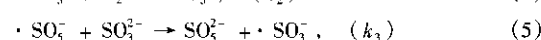
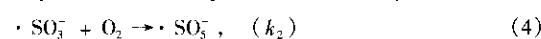
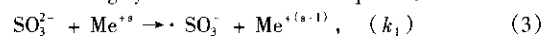
Catalyzed sulfite oxidation has been used to measure gas dispersers and other mass-transfer equipments for about one hundred years. According to the results achieved before, sulfite concentration ranged from 0.2 to 0.8 mol/L and the kinetics of catalyzed sulfite oxidation is extremely complex which has many features in common of solution phase free radical reactions. From half of 1970s, sulfite oxidation was paid more attention to for its use in waste product oxidation of FGD process within the air pollution. In the case of calcium-based scrubbing the sulfite ion concentrations will be low because of precipitation of calcium sulfite. Therefore only investigations on very diluted sulfite solutions are relevant for the oxidation in calcium-based scrubbing slurries under typical FGD conditions. Some of the investigations will be discussed below. Homogeneous system with sulfite concentration from zero to 0.007 mol/L was studied as well as heterogeneous system. Of the systems, only gas-liquid mass transfer and sulfite oxidation exist in homogeneous system, while the process of dissolve, oxidation and crystallization coexists in heterogeneous system, which is the main difference between homogeneous system and heterogeneous system.

1 Mechanism

In aqueous slurry, calcium sulfite forced oxidation mainly appears in liquid phase. The oxidation reactions are generally described as follows (Srivastava, 1968; Mishra, 1976; Linek, 1981):



In fact, they are a sequence of very complex free radical reactions involving a number of highly reactive intermediate species:

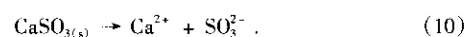


Of the radical reactions, it is assumed that the Reaction (4) is rapid which would not constraint the total reaction rate, the reactions are terminated by radical species combination in Reaction (7), and Reaction (8) keeps thermodynamic equilibrium during oxidation. So it can be derived that the oxidation rate expression by using the steady-state approximation:

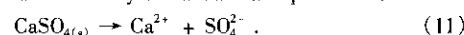
$$r = kc_{\text{Me}^{*s}}^{1/2} c_{\text{SO}_3^{2-}}^{3/2} c_{\text{O}_2}^0, \quad (9)$$

$$\text{where, } k = k_3 \left(\frac{k_1}{k_5} \right)^{1/2}.$$

Moreover, the concentration of sulfite in aqueous slurry containing calcium is governed by the following equilibrium only as long as the concentration of calcium sulfate (final product) is below its precipitation level:



With the concentration of calcium increasing due to the formation of more soluble calcium sulfate, the concentration of SO_3^{2-} diminishes to achieve the minimum value fixed by the additional equilibrium:



So it can be predicted that dissolve, oxidation, and crystallization appear together during forced oxidation of aqueous slurry.

2 Experimental apparatus and procedure

The experiments were carried out in homogeneous system and in

heterogeneous system. The former was done to determine the rate expression for calcium sulfite in solution. The lab scale experimental apparatus were thermostatic stirring tanks for semi-batch process and continuous flow process (Fig. 1 and Fig. 2). The semi-batch process consists of a mechanically agitated thermostatic reactor, which is a 1000 ml volume flask. The flask has five necks for a continuous feeding of gas and a batch of solution/aqueous slurry. In the continuous flow process, the main reactor is made of Pyrex glass, which is a jacketed, and 0.13 m ID cylinder with a hemispherical bottom. In both processes, an axial stirrer was used to provide thorough mix in liquid/aqueous slurry. The stirrer blade is 0.03 m width and 0.06 m impeller diameter. The temperature was set at 45°C in all experiments. Air was bubbled into the bottom of the reactor and then up through solution/aqueous slurry at a flow rate of 3 L/min measured by a rotameter. In continuous flow system, the liquid flow rate was kept constantly at 50 ml/min by a peristaltic pump, and the gas flow gave a liquid holdup volume of $3.9 \times 10^{-4} \text{ m}^3$. The residence time of solution/aqueous slurry in continuous flow system is 470s. The stirrer speed n was kept constantly in the experiments as much as 400–500 revolutions per minute.

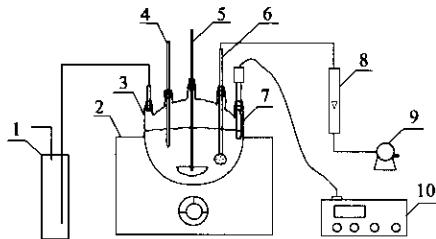


Fig.1 Semi-batch experimental apparatus
1.tail gas absorber; 2.thermostat; 3.flask with five necks; 4.thermometer; 5.electromagnetism constant speed stirrer; 6. gas distributing unit; 7. compound electrode; 8.rotameter; 9.air pump; 10. pH meter

The liquid phases were clear solution or aqueous slurry of calcium sulfite by dissolving analytical calcium hydroxide into deionized water, and then they contacted with pure SO₂ with the controlled pH value in the range of 3.0–6.0. The concentration of Ca²⁺ and total SO₃²⁻ both ranged from 10⁻³ to 0.024 mol/L. In the experiments, manganous sulfate has been selected as the catalyst. Manganese is one of the minor coal elements which can be transferred from coal to ash, condensed phase and flue gas during the coal combustion. In FGD system, manganese ion is the secondary rich metal ion besides iron ion. According to the measurement of FGD system of some Hangzhou Power Station and literatures data (Weisnicht, 1980; Yan, 1999), the concentration of manganese in FGD system can reach to the magnitudes of 10⁻³ mol/L. After calcium sulfite oxidation, it would enter into waste water system for further treatment which is not the topic included in this study. The concentration of manganese was varied in the range of 0–0.1 mol/L.

At the beginning of each experiment, as the liquid in the reactor reached 45°C, sulfur dioxide was fed into solution/aqueous slurry with stirring until pH value descending to 5–6 when calcium sulfite solution/aqueous slurry was produced. Then, air was introduced immediately and oxidation started in semi-batch system. Especially in continuous flow system, as soon as the liquid or aqueous slurry in the reactor reached overflow, agitation was started and air was introduced.

The oxidation rate of calcium sulfite was determined by measuring total sulfite concentration in solution/aqueous slurry by iodometric titration using starch as an indicator, while calcium ion concentration was measured by EDTA titration using murexide as an indicator. Sulfate ion in solution was measured by DX-80 IC, and in slurry by the standard

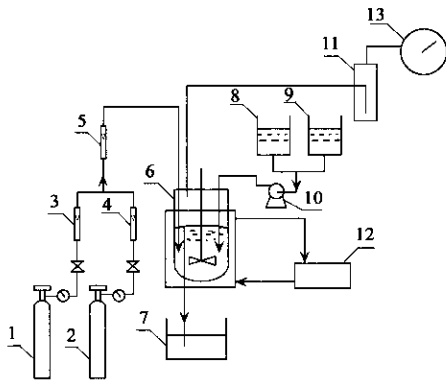


Fig.2 Continuous flow experimental apparatus
1,2. gas cylinders (O₂, N₂); 3, 4, 5. rotameters; 6. reactor; 7,8.slurry tank; 9.catalyst solution tanks; 10.peristaltic pump; 11.tail gas absorber; 12.thermostat; 13.wet flowmeter

BaSO₄ precipitation method. The precipitates formed in experiments were observed under microscope in polarized light.

3 Experimental results

3.1 Catalyzed oxidation of calcium sulfite in semi-batch system

Results of typical calcium sulfite oxidation shown at discrete times are presented in Table 1 and Fig. 3 and 4. The relations between oxidation rate and total calcium sulfite(solid and liquid in heterogeneous system) and catalyst concentration are shown in Fig. 5 and 6 respectively.

$r_{\text{oxide}} \times 10^5$ with different C_{Mn} and C_{sulfite} in semi-batch system							
r_{oxide} , mol/(L·min)	C_{sulfite} , mol/L	C_{Mn} , mol/L					
		0.00	1.00E-5	1.00E-4	1.00E-3	1.00E-2	1.00E-1
0.0023	6.04	4.82	18	18	18	18	
0.0046	7.54	21.8	30.8	30.8	30.8	30.2	
0.0070	10.35	23.2	30.2	37.2	38.6	51.5	
0.0122	18.84	33.0	45.8	42.4	49.4	50.2	
0.0235	13.33	29.5	32.5	40.0	44.3	53.6	
0.0774	25.18	38.5	48.1	49.0	61.0	–	–

In homogeneous system, experiments showed that the oxidation rate is the highest initially, and then descends sharply with sulfite consuming without catalyst(Fig.3 and Fig.5). The oxidation rate is around $6.04 \times 10^{-5} \text{ mol/(L·min)}$ at sulfite concentration of 0.0023 mol/L, while $5.57 \times 10^{-6} \text{ mol/(L·min)}$ at half of the initial concentration(Fig.5). There are also a series of experiments performed by using different manganese concentrations between 10⁻⁶ to 0.1 mol/L without pH control, and experimental results indicate that manganese has a significant effect on the oxidation at low concentrations($C_{\text{sulfite}} < 7 \times 10^{-3} \text{ mol/L}$, and $C_{\text{Mn}} < 10^{-4} \text{ mol/L}$), shown in Table 1 and Fig.4. While manganese effect is weakened with its concentration increasing further.

Oxidation in heterogeneous system is different from that in homogeneous system for the existence of solid particles. Calcium sulfite concentration in solution exceeds 0.007 mol/L when solid particles appear. Experimental results indicated that calcium sulfite oxidation is easier in heterogeneous system than in homogeneous system. Especially during the oxidation, the rate can be kept at $5 \times 10^{-4} \text{ mol/(L·min)}$ constantly (Fig. 5), which is two magnitudes higher than that in homogeneous system. However, thorough oxidation in heterogeneous system without catalyst needs also long time for slow final oxidation rate with the consumption of calcium sulfite. For heterogeneous system,

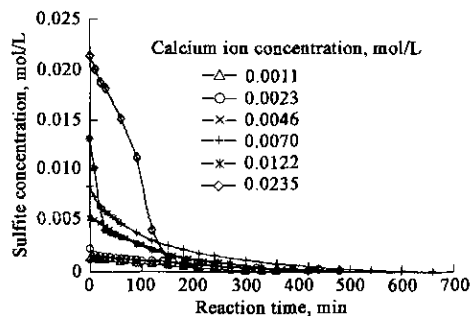


Fig. 3 Sulfite versus time without manganese added in semi-batch system

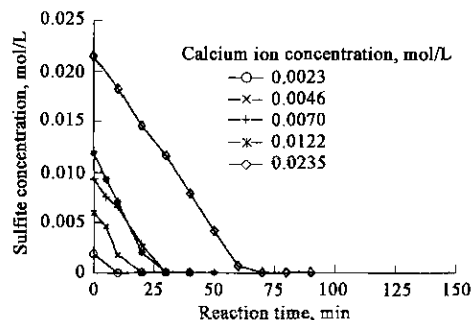
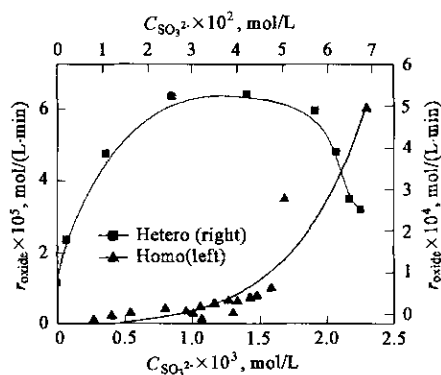
Fig. 4 Sulfite versus time with manganese of 10^{-4} mol/L in semi-batch system

Fig. 5 Oxidation rate varies with sulfite concentration without manganese in homogeneous and heterogeneous systems in semi-batch system

catalyst has only limited effect on the oxidation.

Moreover, it can be observed (Fig. 6) that there are three subsections during catalyst concentration rising. In subsection (a), oxidation rate increases with catalyst concentration increasing; in subsection (b), catalyst effect is weakened; and in subsection (c), the feature is the same as in subsection (a), even the rate is more fast than that in subsection (a). In fact, catalyzed oxidation of calcium sulfite undergoes the changes from chemical kinetics to mass transfer with Mn^{2+} increasing.

The pH value changes are shown in Fig. 7 during calcium sulfite oxidation in homogeneous and heterogeneous systems with or without manganese. Without manganese, pH values descend to around 4 no matter that the oxidation is in homogeneous or heterogeneous system. While with manganese, the final pH values are both in the vicinity of 2.9. Moreover, pH values change is different between homogeneous system and heterogeneous system. In homogeneous system, pH values decrease directly with oxidation; while in heterogeneous system, there exist flat steps during oxidation.

3.2 Catalyzed oxidation of calcium sulfite in continuous flow system

In continuous flow system, there are also different series of experiments carried out to measure the catalyzed oxidation of calcium

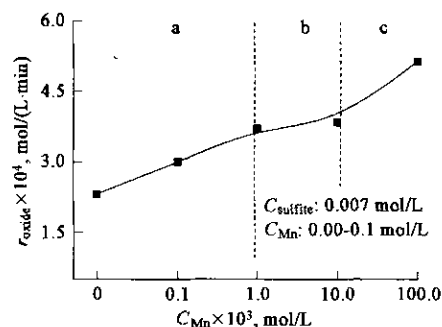


Fig. 6 Oxidation rate versus manganese concentration at turning point of calcium sulfite concentration

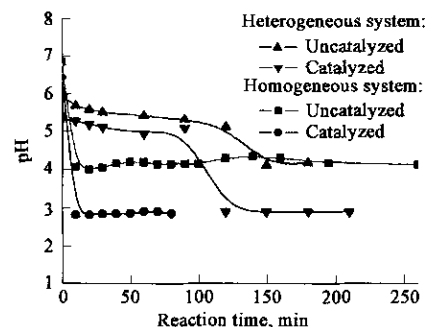


Fig. 7 Typical pH versus reaction time in homogeneous and heterogeneous system

sulfite. The results are reported in Fig. 8 and Fig. 9 and Table 2.

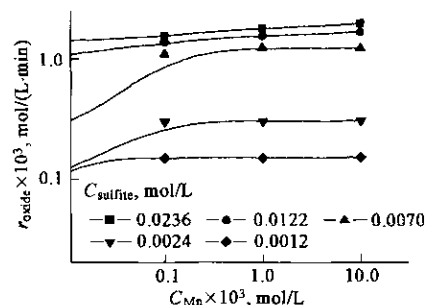


Fig. 8 Effect of manganese concentration on calcium sulfite oxidation in continuous flow system

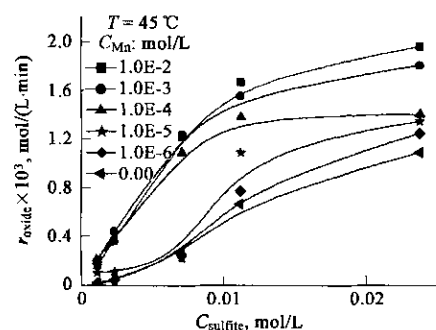


Fig. 9 Effect of sulfite concentration on calcium sulfite oxidation in continuous flow system

Catalyst effect in heterogeneous system is as the same as that in homogeneous system. However, in Fig. 8, the oxidation rate is reported in a logarithmic plot as a function of manganese concentration which shows that the oxidation rate increases with manganese until an upper

limit is reached, at which the rate becomes almost independent of manganese concentration especially when its concentration is up to the turning point 10^{-4} mol/L. Fig.9 indicates that manganese particularly influences the oxidation rate at relatively low sulfite concentrations($C_{\text{sulfite}} < 0.007$ mol/L). Table 2 shows the rates under different manganese concentrations. The results from continuous flow system are in agreement with those from semi-batch system.

Table 2 $r_{\text{oxide}} \times 10^4$ with different C_{Mn} and C_{sulfite} in continuous flow system

r_{oxide} , mol/(L·min)	C_{Mn} , mol/L					
	0.00	1.00E-6	1.00E-5	1.00E-4	1.00E-3	1.00E-2
C_{sulfite} , mol/L						
0.0012	0.21	0.25	1.51	1.51	1.51	1.51
0.0024	0.46	0.53	1.17	3.02	3.02	3.02
0.0070	2.56	2.52	2.25	10.9	12.40	12.20
0.0118	6.73	7.78	10.90	13.90	15.60	16.70
0.0235	11.00	13.60	14.20	15.6	18.20	19.70

3.3 Oxygen concentration

The effect of oxygen concentration on oxidation is shown in Fig.10 and Fig.11.

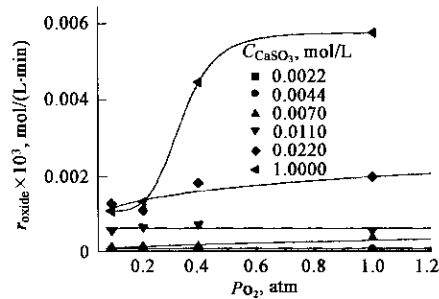


Fig.10 Oxidation rate versus oxygen concentration without manganese in continuous flow system

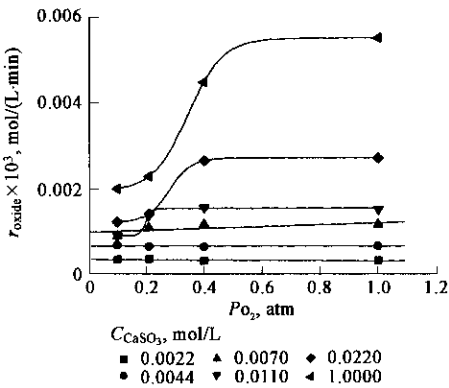


Fig.11 Oxidation rate versus oxygen concentration with $C_{\text{Mn}} = 10^{-4}$ mol/L in continuous flow system

The results reported in Fig.10 and 11 showed that the reaction rate hardly depends on the oxygen partial pressure, especially at low calcium sulfite concentration (0–0.007 mol/L) and low oxygen concentration (below 0.4 atm). While the effect of oxygen concentration on the oxidation is more obvious with manganese than that without manganese. For high oxygen concentration(exceeding 0.4 atm), the effect of oxygen can not be neglected.

4 Discussion

4.1 Sulfite concentration

For sulfite concentration, the reaction order of 1.5 is just relevant

for very diluted sulfite solution in the case of calcium based FGD slurry for precipitation of calcium sulfite (Bengtsson, 1975). Literature data indicated that the reaction order of sulfite is 0—1.5 in both uncatalyzed (Amedeo, 1996) and catalyzed systems (Amedeo, 1999a; 1999b; Zhong, 2000). In this research, there is a regressive line graphed in Fig.12 and corresponding the regressive line Equation (12) is gained:

Igt_{1/2} = 0.6779 – 0.5094lg C₀. (12)

The slope of the line represents the value of 1 subtracting the reaction order of calcium sulfite, so calcium sulfite order can be obtained as 1.5, which is consistent with the theory value and some literature data. In this research, 1.5 order fits the range of calcium sulfite concentration from zero to 0.007 mol/L, namely in homogeneous system.

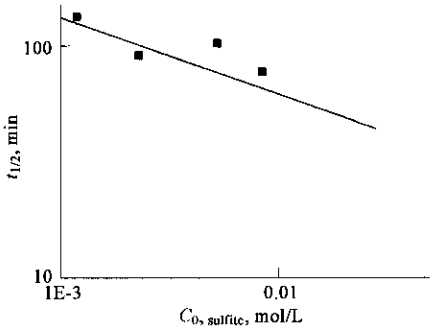


Fig.12 Rate of sulfite consumption as a function of 1.5th at low sulfite concentration

Heterogeneous system is different from homogeneous system for dissolve, oxidation and crystallization co-existing. The constituents distribution in solution is also determined by the co-existing processes. Fig.5 indicates that there exists an inducing process before equilibrium state formation when sulfate ion concentration is kept at a certain supersaturated level which is about 1.5 measured in the experiments, and sulfite ion concentration is at a minimum level for the dynamic balance between reactions and calcium sulfite dissolve from solid particles. So the reaction rate can be maintained constantly until calcium sulfite in solid particle is used up. Then the change of reaction rate is similar to that of homogeneous system.

4.2 Manganese concentration

For calcium sulfite oxidation, on the one hand, it is a series of complex free-radical reactions expressed as Reaction (3)—(8). Of the reactions, Reaction (3) is the free-radical initiation in which $\cdot\text{SO}_3^-$ is produced and becomes the key constituent for propagation of the chains for whole reactions. On the other hand, gas film resistance is negligible and liquid film resistance is the main factor during oxygen absorption. In uncatalyzed system and with low manganese concentration($< 10^{-5}$ mol/L), sulfite concentration in the vicinity of interphase is smaller than that in the bulk. Simultaneously, in the section of interphase sulfate ion is accumulated which prevents oxygen from dissolving and transferring (Linek, 1981). At the same time, equilibrium concentration of sulfite determined by Reaction (10) and (11) is achieved at its minimum value. Then Reaction (3) and (4) are both held up which results in a sharp decrease of pH value and chemical rate. Thereafter oxygen is accumulated in liquid phase which blocks oxygen transfer further as well as sulfate ion in solution, and the reaction rate appears independently on oxygen concentration just as Equation (9) described. In catalyzed system, with manganese concentration increasing, Reaction (3) and (4) are both assured. Oxygen would be exhausted for the rapid Reaction (4), and further oxygen transfer is enhanced. The effect of catalyst on Reaction (3) exceeds greatly the mass transfer resistance brought by

sulfate ion accumulation, so the accumulated sulfate appears no significant effect on oxidation. The turning point of manganese concentration is 10^{-4} mol/L, when oxidation becomes less dependent on manganese concentrations (Table 1 and 2) but more on oxygen concentration, shown in Fig. 11 (Pasiuk, 1985; Linek, 1970; Nyvlt, 1975).

According to experimental results, it is achieved that the reaction order of manganese is 0.5 at low manganese concentration, shown in Fig. 13. It indicated that when manganese concentration exceeds the concentration of 10^{-4} mol/L, reaction rate reaches the upper limit where it no longer depends on manganese concentration. Oxidation process enters into diffusive regime (Amedeo, 1999a; 1999b).

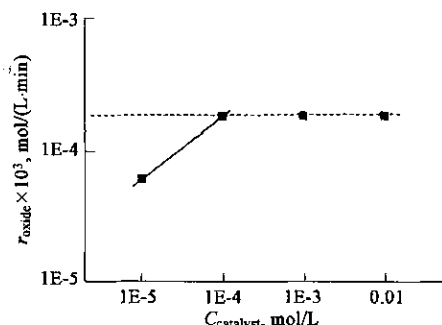


Fig.13 Rate of sulfite consumption as a function 0.5th at low sulfite and manganese concentration

4.3 Oxygen concentration

There were not consistent conclusions about the effect of oxygen concentration on the calcium sulfite oxidation by different authors. It has been proved that low oxygen concentration hardly influences calcium sulfite oxidation. For high oxygen concentration, it may play a role, albeit indirectly, by determining the transition from the kinetic subregime to the diffusive subregime. So the oxygen effect more likely reflects two different diffusive controlled steps of the chain reaction mechanism. The two diffusive steps are: (1) Free radical chain propagation—the step (4) in the reaction sequence; (2) catalyst regeneration: reduced state catalyst species are oxidized to active species again—the step (8) in the reaction sequence. So it needs to know about the relation between the transfer process among different phases interface and the chemical kinetics mechanism accurately just described as section 4.2, then the effect of oxygen concentration can be described properly (Amedeo, 1996).

4.4 pH value

In this work, pH value during the oxidation was not controlled and its change reflects different liquid constituents in homogeneous and heterogeneous systems with or without manganese. In fact, the flat steps in heterogeneous system shown in Fig. 7 correspond to the constant reaction rate shown in Fig. 5. The phenomena indicated that liquid constituents can be kept constantly in aqueous slurry. According to the theoretic analysis and experimental observation, they are the results of the co-existence of dissolve, oxidation and crystallization in aqueous slurry. After the inducing step, sulfate ion in solution is kept at a supersaturated level of 1.5 times with continuous crystallization, and sulfite ion is kept at a steady minimum concentration balanced by consumption and dissolve. The dynamic balanced state is maintained until calcium sulfite of solid particle is used up. Then the pH value reaches the second break.

5 Conclusions

The oxidation of calcium sulfite aqueous slurry containing manganese by air is a useful reaction in the study of the calcium-based FGD process. The oxidation is a series of complex free-radical reactions which are influenced greatly by manganese as catalyst. The analysis of the experimental results is made complex by the problem of individuating the region in which oxygen absorption takes place. At low calcium sulfite and manganese concentrations, the reaction rate is proportional to 1.5 order of calcium sulfite, 0.5 order of manganese and zero order of oxygen. However, there exist critical concentrations above which the reaction rate would be independent on calcium sulfite and manganese concentrations, while dependent on oxygen concentration. The critical concentration of calcium sulfite is 0.007 mol/L, manganese is 10^{-4} mol/L, and oxygen is of 0.2–0.4 atm.

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