



Dissolution rate of limestone for wet flue gas desulfurization in the presence of sulfite

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ABSTRACT

Limestone dissolution rate was measured by a pH-stat method with CO₂ sparging and dissolved sulfite. The dissolution rate of limestone under these conditions was found to be controlled by mass transfer and surface kinetics. As can be seen from the results, in the presence of sulfite, limestone dissolution rate increases with increasing stirring speed, reaction temperature and CO₂ partial pressure. The crystallinity of limestone has a great impact on the dissolution rate: The lower the value of the crystallinity of limestone is, the higher the dissolution rate is. The presence of sulfite promotes the dissolution rate when pH value is below 5.5 but inhibits it when pH value is above 5.5.

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1. Introduction

Limestone-based wet flue gas desulfurization (WFGD) technology has been considered as the most effective method for the control of SO₂ from coal fired boilers. In this process, limestone dissolved in the slurry reacts with absorbed SO₂ to form the solid byproduct: Calcium sulfite and/or gypsum. So the prediction of limestone dissolution rate is very important for optimization of the design and operation of WFGD facilities.

Many researchers have studied the dissolution mechanism of limestone in aqueous solutions. Toprac and Rochelle [1] found that there is no effect of limestone type and particle size distribution is the most important influence factor of limestone dissolution. Chan and Rochelle [2], Wallin and Bjerle [3] and Allers et al. [4,5] studied the dissolution rate of limestone in a pH-stat apparatus under various conditions and reported that the dissolution process can be successfully simulated by mass transfer model combined with the effects of several equilibrium acid/base reactions and the finite reaction of CO₂ and H₂O in the boundary layer. Other researchers found that surface reaction may also affect the dissolution process of limestone. Lund and Fogler [6] studied limestone dissolution in hydrochloric acid using rotating apparatus and found that at –15.6°C both mass transfer and surface reaction can control the

dissolution rate. Bjerle and Rochelle [7] also observed surface reaction kinetics control mode for plane surfaces of limestones using a pH-stat apparatus with CO₂ sparging.

Some species in WFGD system such as SO₃²⁻ may affect the dissolution rate of limestone. Chan and Rochelle [2] indicated that limestone dissolution is enhanced at low sulfite concentration but inhibited at high concentration. Jarvis et al. [8] found that sulfite can seriously inhibit limestone dissolution but the inhibition magnitude is independent of limestone type. Gage and Rochelle [9] showed that limestone dissolution in the presence of sulfite is controlled by a combined surface kinetics/mass transfer mechanism. A surface rate relation including a stone dependent rate constant k_c is given as follows:

$$\text{flux} = k_c \frac{(\text{CaCO}_{3\text{eq}}^0 - \text{CaCO}_{3\text{s}}^0)^{0.5}}{\text{CaSO}_{3\text{s}}^0 \text{CaCO}_{3\text{s}}^0} \quad (1)$$

The objective of this work is to study the effects of limestone microstructure, pH, stirring speed, reaction temperature and CO₂ partial pressure on limestone dissolution rate in the presence of sulfite.

2. Dissolution model

Assuming limestone particle is nonporous and spherical, the dissolution flux of a single particle can be given by

$$\text{flux} = \frac{\rho_m}{\pi d^2} \frac{dV}{dt} \quad (2)$$

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Nomenclature

C_b	bulk concentration of H^+ (mol/m ³)
C_b^*	equilibrium surface concentration of H^+ (mol/m ³)
d	diameter of a spherical limestone particle (m)
d_i	diameter of a limestone particle from size fraction at a given time (m)
d_{oi}	initial diameter of a spherical limestone particle from size fraction i (m)
e	porosity of limestone
E	activation energy (kJ/mol)
F	fraction of dissolved limestone sample
FWHM	half-peak width (°)
k	dissolution rate constant (m/s)
k_0	pre-exponential factor (m/s)
k_c	surface reaction rate constant (mol ^{5/2} /(m ^{13/2} s))
N_i	number of limestone particles from size fraction i
R	universal gas constant (kJ/(mol k))
T	temperature (K)
t	time (s)
t_{50}	time required to dissolve 50% of the limestone (s)
t_{55}	time required to dissolve 55% of the limestone (s)
V	volume of a spherical limestone particle (m ³)
V_{oi}	initial volume of a particle from size fraction i (m ³)
V_{tot}	total volume of limestone particles (m ³)

Greek letters

ϕ_i	volume fraction of limestone particles between size i and $i + 1$
ρ_b	bulk density of limestone (kg/m ³)
ρ_m	molar concentration of CaCO ₃ and MgCO ₃ in limestone (mol/m ³)

Subscripts

eq	equilibrium
o	initial
s	surface

For polydispersed limestone particles, the dissolution flux is given by [9]

$$\text{flux} = \frac{\rho_m V_{tot}}{\Sigma \pi d_i^2 N_i} \frac{dF}{dt} \quad (3)$$

d_i in Eq. (3) can be calculated by

$$d_i = d_{oi} \left(1 - \frac{\omega t}{d_{oi}} \right) \quad (4)$$

where ωt is a parameter which can be found by iteration using the following equation until the desired utilization is reached:

$$F = \Sigma \phi_i \left(1 - \frac{\omega t}{d_{oi}} \right)^3 \quad (5)$$

The number of particles from size fraction i could be written as

$$N_i = \frac{V_{tot} \phi_i}{V_{oi}} \quad (6)$$

Once ωt is found from Eq. (5) at a given utilization, the area of limestone particles from each size fraction can be determined by Eqs. (4) and (6), then the dissolution flux of the limestone sample can be calculated by Eq. (3).

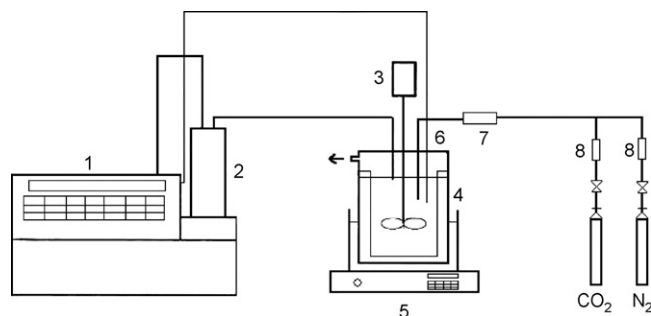


Fig. 1. Schematic of experimental apparatus: (1) autotitrator, (2) HCl bottle (3) stirrer, (4) reactor, (5) water bath, (6) pH electrode, (7) mixer, and (8) mass flowmeter

3. Experiment

Limestone dissolution experiments were performed in a pH-stat apparatus, as shown in Fig. 1. The pH was automatically controlled to ± 0.02 by titrating with 1 M HCl. The dissolution rate of limestone is related to the following stoichiometry:



Experiments were carried out in 500 ml solution contained in 800 ml reactor. The reaction temperature was controlled $\pm 0.5^\circ C$ by using a water bath. During the experiments, presaturated CO₂ was sparged through the solution solely or mixed with pure N₂ at a rate of 400 ml/min. To keep a constant ionic strength and reduce changes in solution concentration as the limestone dissolved, all experiments were performed in a background solution of 0.1 M CaCl₂ [9,10]. A two-blade impeller rotating at 300–700 rpm was used to agitate the solution.

Natural limestones from four different mines of China were used in the experiments. The contents of soluble component (CaCO₃ and MgCO₃) and physical properties are listed in Table 1. The raw limestone sample were ground and sieved into different size ranges. Samples with the particle size between 38.5 and 43.5 μm were used in the experiments. Their particle size distribution were measured by a Mastersizer 2000 laser particle sizer using ethanol as dispersant agent, then the values of d_{io} and ϕ_i used in the dissolution model were obtained too.

The physical properties such as porosity, bulk density and molar density of the four limestones were measured and are shown in Table 1. As can be seen from Table 1, the porosities of the four limestones are very small and thus can be seen as nonporous.

At the beginning of the experiment, 500 ml CaCl₂ solution was heated to the desired temperature. Then CO₂ or the mixture of CO₂ and N₂ was sparged through the solution for about 30 min to pre-saturate the solution. After that, 1 g of limestone sample was added to the solution. Then sodium sulfite was added to get the desired concentration (1 mM) and confirmed by iodometric titration. During the experiment, this concentration was checked every half an hour. If there was a drop in sulfite concentration caused by oxidation to sulfate, additional sulfite was added as Na₂SO₃/NaHSO₃ buffer solution at the pH of the experiment. Thus the concentration of sulfite was kept within $\pm 5\%$ of the desired value throughout

Table 1
Soluble component contents and physical properties of limestones.

Limestone origin	CaCO ₃ (wt.%)	MgCO ₃ (wt.%)	ρ_b (kg/m ³)	e	ρ_m (mol/m ³)
Banshan	99.07	0.57	2632	0.02	26523.82
Fugu	92.48	4.94	2617	0.07	25741.06
Lanxi	96.25	0.53	2664	0.05	25809.09
Qianqing	97.07	1.05	2624	0.03	26192.45

Table 2
Effect of limestone type on its dissolution rate in the presence/absence of sulfite.

Limestone origin	Banshan	Fugu	Lanxi	Qianqing
Flux in the absence of sulfite (mol/(m ² s))	4.53×10^{-4}	4.90×10^{-4}	4.33×10^{-4}	4.33×10^{-4}
Flux in the presence of 1 mM sulfite (mol/(m ² s))	4.04×10^{-4}	4.23×10^{-4}	3.19×10^{-4}	2.54×10^{-4}
FWHM	0.214	0.220	0.211	0.207

the experiment. At the end of a run, the sulfite concentration was checked again to confirm that the value was still in the error range. The dissolution fraction of limestone F was obtained by the ratio of the HCl volume added to that required for complete dissolution.

dF/dt in Eq. (3) was calculated by the following equation with the measured values of t_{50} and t_{55} :

$$\frac{dF}{dt} = \frac{0.05}{t_{55} - t_{50}} \quad (8)$$

Then the dissolution rate of limestone sample can be calculated by Eq. (3).

4. Results and discussion

4.1. Effect of limestone microstructure on its dissolution rate in the presence of sulfite

The dissolution rate of the four limestones at 55 °C, pH 5.5, stirring speed 500 rpm, particle size 38.5–43.5 μm in the absence and presence of sulfite is shown in Table 2. It is clear that limestone dissolution rate in the absence of sulfite has little relation to its type in the error range, which is in consistent with the conclusion of Rochelle and Chan [11] and Shih et al. [10]. Although the MgCO₃ content in Fugu limestone is near 5 wt.%, XRD results show that the existing form of Mg in Fugu limestone is dolomite, as is shown in Fig. 2. Therefore, it is different from the conclusion of Ahlbeck et al. [12] that the presence of Mg has no inhibition effect on limestone dissolution rate. This is due to the fact that limestone dissolution in the absence of sulfite is in mass transfer control regime under the experimental conditions. It is noteworthy that the time taken to reach a certain dissolved fraction for limestone depends on the limestone origin and its initial particle size distribution because the required time is proportional to the content of CaCO₃ and MgCO₃ in the limestone and the surface area of the limestone. Gage and Rochelle [9] indicated that, in the presence of sulfite, surface reaction rate constant for limestone dissolution is dependent on limestone type. In this study, the effect of limestone

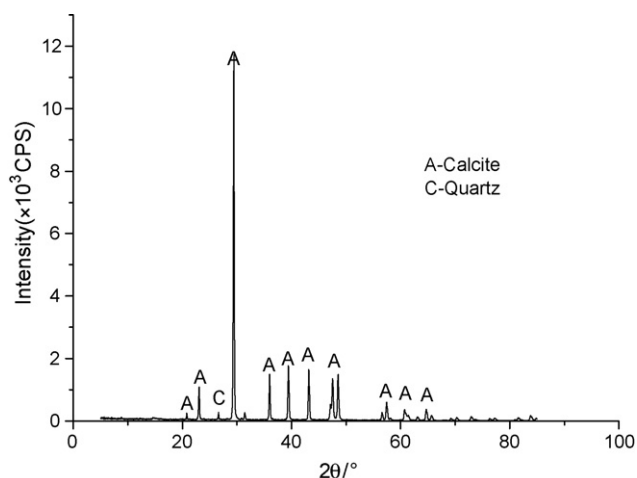


Fig. 2. XRD spectrum of Banshan limestone.

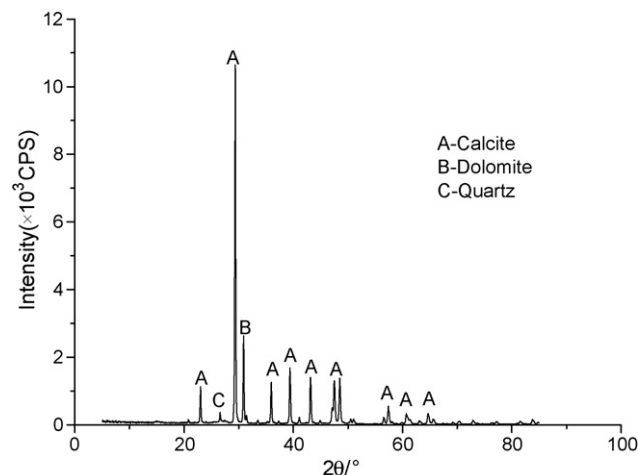


Fig. 3. XRD spectrum of Fugu limestone.

microstructure on its dissolution rate in the presence of sulfite is investigated. The XRD spectrums of the four limestones are shown in Figs. 2–5. The half-peak widths of the four limestones are listed in Table 2. It is well known that the degree of crystallinity of limestone is inversely proportional to its half-peak width. As can be seen from Table 2, Fugu limestone, which has the maximum half-peak width and thus the lowest degree of crystallinity, has the highest dissolution rate for the four limestones under the same conditions. On the other hand, Qianqing limestone, which has the highest crystallinity, has the lowest dissolution rate. Therefore, the crystallinity of limestone has great effect on its dissolution rate.

Since the Fugu limestone has highest MgCO₃ content, it may have some effect on limestone rate. While the existing form of Mg in Fugu limestone is dolomite, previous researchers had found that dolomite is insoluble under WFGD conditions [13], so the highest dissolution rate could not be attributed to its highest MgCO₃ content.

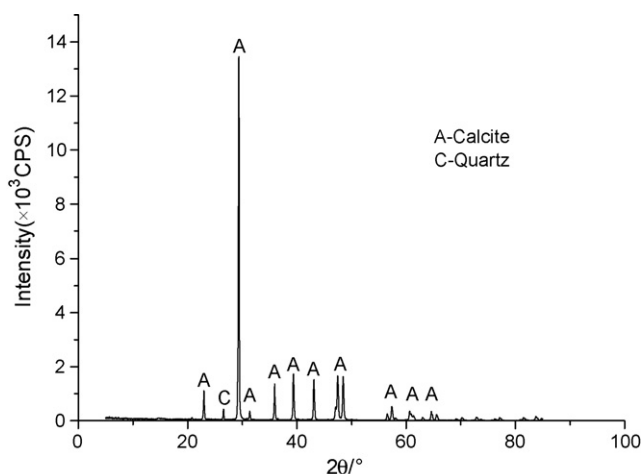


Fig. 4. XRD spectrum of Lanxi limestone.

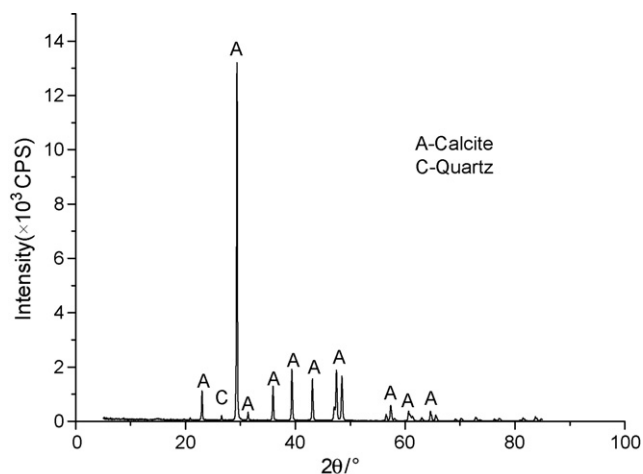


Fig. 5. XRD spectrum of Qianqing limestone.

4.2. Effect of pH on limestone dissolution rate

Fig. 6 shows the effect of pH on Banshan limestone dissolution rate in the presence and absence of sulfite. It is clear that lower pH is favorable to the dissolution of limestone. This is because the gradient of H^+ between liquid bulk and limestone surface is the important driving force for limestone dissolution. But limestone dissolution process in the presence of sulfite is not controlled solely by mass transfer. Ahlbeck et al. [12] had indicated that, for limestone dissolution in acid solution, the concentration of H^+ in the liquid bulk is much greater than that at the limestone surface and the surface concentration of H^+ can be taken as zero. As can be seen from Fig. 6, when pH increases from 4 to 4.5, the gradient of H^+ between liquid bulk and limestone surface reduces by 68.4%, while the dissolution rate reduces about 63.3% (from 1.02×10^{-2} to 3.74×10^{-3} mol/(m² s)). In addition, when pH is lower than 5.5, sulfite seems to promote limestone dissolution because of the buffer effect of HSO_3^-/SO_3^{2-} at the limestone surface by providing H^+ consumed during the dissolution reaction. When pH is higher than 5.5, the inhibition effect of sulfite on limestone rate is more apparent, which is also observed by Chan and Rochelle [2], thus the promotion effect and inhibition effect of sulfite on limestone dissolution would offset each other. As a result, sulfite seems to have no effect on limestone dissolution in the pH range of 5.5–6.0 under the experimental conditions.

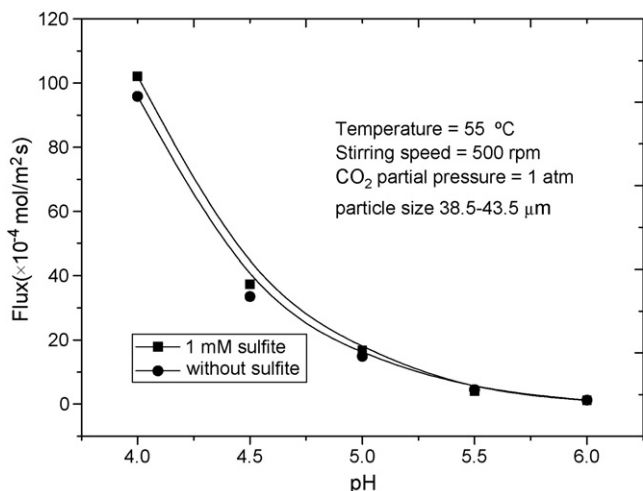


Fig. 6. Effect of pH on limestone dissolution rate in the presence/absence of sulfite.

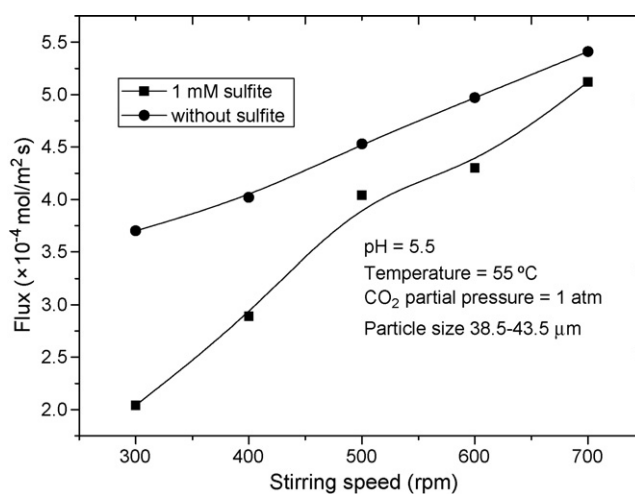


Fig. 7. Effect of stirring speed on limestone dissolution rate in the presence/absence of sulfite.

4.3. Effect of stirring speed on limestone dissolution rate in the presence of sulfite

Fig. 7 shows the effect of stirring speed on Banshan limestone dissolution rate in the presence and absence of sulfite. The observed dissolution rate increases with increasing stirring speed. This is due to the enhancement of mass transfer caused by the agitation. Many researchers had studied the effect of agitation on liquid mass transfer between liquid and suspended particles. Calderbank and Moo-Young [14] found that convective liquid mass transfer resulted from the turbulence in the surrounding fluid is independent of particle and is affected by specific agitation power. Harriott [15] reported that mass transfer coefficient increases with decreasing particle size for small particles, but when the particle size is larger than 100 μm , mass transfer coefficient is proportional to 0.5 power of the stirring speed. In this study, the increase of stirring speed enhances the convective mass transfer between liquid and limestone particles, thus promoting the dissolution of limestone. In addition, the effect of stirring seems more obvious for limestone dissolution in the presence of sulfite. This may be due to the fact that mass transfer has a greater impact on limestone dissolution at a lower stirring speed.

4.4. Effect of reaction temperature on limestone dissolution rate in the presence of sulfite

Fig. 8 shows the effect of reaction temperature on Banshan limestone dissolution rate in the presence and absence of sulfite. It reveals that limestone dissolution rate increases with increasing temperature and the effect is quite significant. It is generally accepted that a diffusion-controlled process is slightly dependent on temperature and a chemical reaction controlled process is strongly dependent on temperature [16]. That is to say, surface reaction plays an important role in the dissolution process in this experiment. To determine the dissolution mechanism of limestone, the activation energies of limestone dissolution in the presence/absence of sulfite are calculated as following.

The dissolution rate of limestone can also be expressed by

$$\text{flux} = k(C_b - C_s^*) \quad (9)$$

where k is the dissolution rate constant, C_b is the bulk concentration of H^+ and C_s^* is the surface concentration of H^+ . According to Ref. [12], for limestone dissolution in an acid solution, C_s^* can be taken

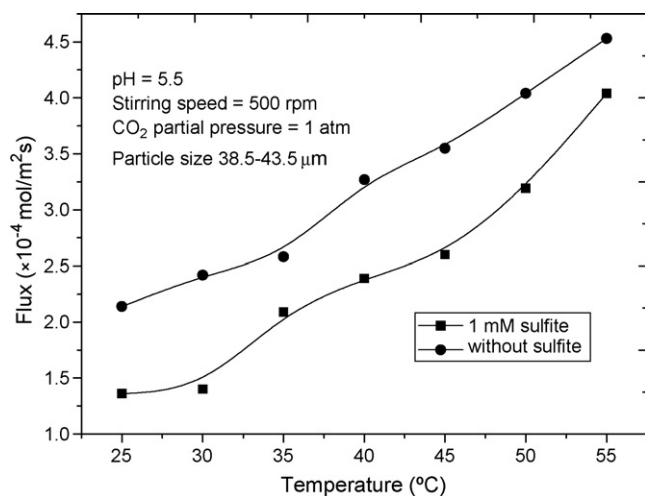


Fig. 8. Effect of reaction temperature on limestone dissolution rate in the presence/absence of sulfite.

as zero. Thus k can be calculated by the following equation:

$$k = \frac{\text{flux}}{C_b} \quad (10)$$

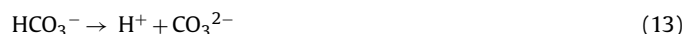
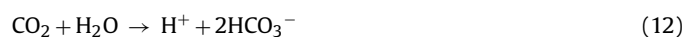
Then the activation energy of limestone dissolution could be obtained by the Arrhenius law:

$$k = k_0 e^{-E/RT} \quad (11)$$

In this equation, k_0 is the pre-exponential factor, E is the activation energy of limestone dissolution reaction, R is the gas constant and T is the temperature. The values of k_0 and E can be obtained from the straight plot $\ln k$ vs. $1/T$. The activation energies of limestone dissolution in the presence/absence of sulfite are 29.81 and 20.88 kJ/mol, respectively. They are all in the range of 20–40 kJ/mol, thus limestone dissolution in the presence/absence of sulfite at pH 5.5 are all under the control by mass transfer and surface kinetics [17]. In addition, the effect of temperature seems more obvious for limestone dissolution in the presence of sulfite; therefore surface reaction plays a more important role in the process of limestone dissolution in the presence of sulfite.

4.5. Effect of CO₂ partial pressure on limestone dissolution rate in the presence of sulfite

Fig. 9 shows the effect of CO₂ partial pressure on Banshan limestone dissolution rate in the presence and absence of sulfite. It is obvious that high CO₂ partial pressure can promote limestone dissolution. The enhancement effect results from the hydrolysis reaction of CO₂:



The upper two reactions produce H⁺, which increases the H⁺ flux towards limestone particle surface. Wallin and Bjerle [3] also observed this phenomenon, compared with dissolution in a nitrogen atmosphere; a high partial pressure of CO₂ can increase the dissolution rate of limestone by a factor of 10. In addition, the enhancement effect is related to the partial pressure of CO₂ within the experimental limits. Lower CO₂ partial pressure seems more effective to enhance the dissolution of limestone.

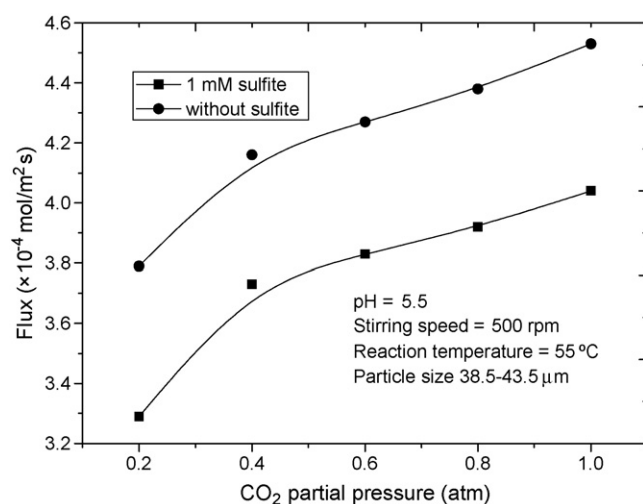


Fig. 9. Effect of CO₂ partial pressure on limestone dissolution rate in the presence/absence of sulfite.

5. Conclusions

The dissolution characteristics of limestone in the presence of sulfite were investigated in a pH-stat apparatus. The study shows that limestone dissolution rate in the presence of sulfite is highly dependent on its crystallinity, pH, stirring speed, reaction temperature and CO₂ partial pressure. And the crystallization properties of limestone should be used as a standard to rank the performance of limestone in flue gas desulfurization process.

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