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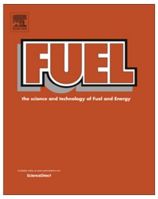

Full Length Article

# The kinetics and pore structure of sorbents during the simultaneous calcination/sulfation of limestone in CFB

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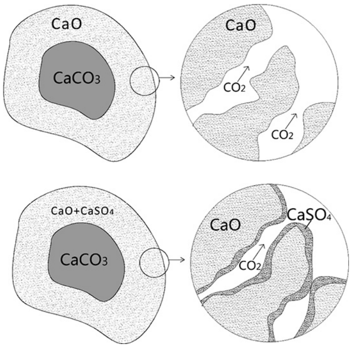
## HIGHLIGHTS

- A constant-temperature reactor was built to study simultaneous calcination/sulfation.
- Calcination and sulphation can be stopped and examined at any time.
- An occlusion phenomenon occurs whereby sulfation delays calcination.
- This is shown from effective diffusion coefficients for $CO_2$ in the presence of $SO_2$.
- The impeding effect of sulfation diminishes at higher temperatures.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The interaction of calcination and sulfation in the simultaneous calcination/sulfation of limestone sorbent under circulating fluidized bed boiler conditions was studied. A specially designed constant-temperature reactor which can stop the reaction at a given time was employed. When limestone entered the furnace of mixed gases of $CO_2$, $O_2$, $SO_2$, etc., its weight went down first, then up, so there was a minimum weight point. The whole reaction period could be divided into two stages by this minimum weight point, named the weight-loss stage and the weight-growth stage, which were dominated by the calcination reaction and by the sulfation reaction, respectively. In the weight-loss stage, the sulfation reaction took place and $CaSO_4$ formed simultaneously together with limestone calcination as long as $SO_2$ was present. In the weight-growth stage, the sulfation ratio at 60 min in simultaneous calcination/sulfation is 30.7% higher than that in the sequential calcination then sulfation process. The weight loss rate of limestone calcined in the presence of $SO_2$ was lower than that without $SO_2$ present but the final weight was higher. The calcination of limestone was slowed by the presence of $SO_2$; a probable mechanism was proposed, namely that the $CaSO_4$ formed may fill or plug the pores in the CaO layer, and impede the transfer of $CO_2$ and, therefore, retard the calcination reaction. This mechanism was supported by the observation that the effective diffusion coefficient of $CO_2$ in CaO produced in the presence of $SO_2$ was reduced. The impeding effect increased with increasing $SO_2$ concentration (0–3000 ppm), while, when the particle size decreased from 0.4–0.45 mm to 0.2–0.25 mm, the calcination rate of limestone was higher, no matter whether there was $SO_2$ present or not. The impeding effect was less pronounced at 880 °C than at 850 °C. The reason for this appears to be the fact that there was less $CaSO_4$ formed at 880 °C and, therefore, fewer pores of the particle were filled or plugged.

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## 1. Introduction

The circulating fluidized bed (CFB) boiler is widely adopted for the combustion of solid fuels like coal, petroleum coke and household waste. In CFBs, limestone is usually used as the in-situ desulfurization sorbent. To capture $SO_2$, limestone goes through both a calcination reaction and a sulfation reaction in the furnace, which can be described by the following global reactions:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1}$$

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \tag{2}$$

Given their great importance, the calcination and sulfation reactions of limestone have been investigated frequently over the past several decades [1–3].

The calcination of $CaCO_3$ is an endothermic reaction, and about 182.1 kJ heat is needed to calcine 1 mol $CaCO_3$ [1]. The decomposition temperature of $CaCO_3$ depends on the $CO_2$ partial pressure in the reaction atmosphere, and the equilibrium $CO_2$ partial pressure ($P$, atm.) at a given decomposition temperature ($T$, K) of limestone can be calculated by the formula of Baker [4]

$$\log P = 7.079 - \frac{8308}{T} \tag{3}$$

The calcination of $CaCO_3$ can be controlled by three steps [5]: heat transfer to the reaction surface, mass transfer of $CO_2$ through the CaO product layer, and the intrinsic chemical reaction. Which of these steps has the most pronounced effect on the reaction rate depends on factors like particle size, temperature, and reaction atmosphere.

Gallagher and Johnson [6] investigated the calcination of 30 μm $CaCO_3$ by thermogravimetric analysis (TGA) at 900–950 °C in a $CO_2$ atmosphere, and found that the reaction rate was determined by heat transport. Caldwell et al. [7] came to the same conclusion in a study comparing the decomposition rate of 30 μm $CaCO_3$ in three different sweep gases (He, Ar and $N_2$) between 550 and 680 °C. However, in a study using small limestone particles and high-speed sweep, Borgwardt [5] found that the limestone calcination reaction rate is independent of heat transfer, and shows an Arrhenius relationship with temperature. The calcination reaction activation energy is about 205 kJ/mol according to Borgwardt [5], which is close to the value (209.5 kJ/mol) obtained by Powell and Searcy [8] in a study calcining a thin calcite crystal in vacuum.

Particle size is another factor that will influence the calcination rate of limestone. The research of Borgwardt [5] found that when particle size increases in the range 1–90 μm, the calcination reaction rate decreased noticeably. Another conclusion of Borgwardt [5] is that the calcination reaction rate is proportional to the initial surface area of the particle. An investigation by Hu and Scaroni [9] indicated that for particles >20 μm and temperatures >1200 °C, external heat transfer and pore diffusion of $CO_2$ are the major causes of reaction resistance, and for particles <10 μm and temperature <800 °C, chemical kinetics is the rate-controlling step.

The calcination reaction rate can also be influenced by the $CO_2$ partial pressure at the reaction surface. The influence of $CO_2$ on calcination rate of $CaCO_3$ was investigated experimentally by Khinast et al. [10], who found that the reaction rate decreased exponentially with increasing $CO_2$ partial pressure. However, other studies found that the reaction rate was inversely proportional to $CO_2$ pressure or the difference between $CO_2$ pressure at the reaction surface and the equilibrium pressure [11,12].

The sulfation reaction rate of CaO can also be influenced by three steps: mass transfer of $SO_2$ through pores to the inner surface of the particle, solid state diffusion of reactant through the compact $CaSO_4$ product layer, and the intrinsic sulfation reaction. Commonly, the sulfation reactions of CaO include two reaction stages, a fast reaction stage controlled by the intrinsic sulfation reaction, and a slow reaction stage controlled by the diffusion of reactant through the $CaSO_4$ layer.

The sulfation reaction rate can be influenced by several factors, like temperature, $SO_2$ concentration, particle size, etc. Many studies have shown that there is an optimum temperature for sulfur capture of CaO in CFBs, around 850 °C [1]. Why there is an optimum temperature for sulfur capture of limestone in CFB is, however, not very clear at present. Particle size is one of the main factors which influence the sulfation rate of CaO significantly. Smaller sizes decrease the $SO_2$ gas transport resistance, and improve the $SO_2$ concentration levels seen in the inner part of the particle. The sulfation behavior of four particle sizes of limestone (158, 353, 632 and 1788 μm) was tested by Adánez et al. [13], and the results showed there was an increase of the sulfation rate with decreasing CaO particle size. A similar conclusion was drawn by Borgwardt [14] in a study on the sulfation of three sizes of CaO particles (96, 250 and 1300 μm). Although fine limestone particles have a high sulfation rate, an excess of fine particles in CFBs will decrease the sulfur capture efficiency because of their short residence time in the furnace. $SO_2$ concentration also influences the sulfation reaction rate, but the reaction order of $SO_2$ obtained by different researchers varies significantly. The study of Simons et al. [15] showed that the sulfation reaction rate of CaO is of the order of 1 for $SO_2$, but the experiments of Borgwardt et al. [16] indicated that the sulfation reaction rate is of the order of 0.64.

One other factor that affects the reactivity and utilization of CaO is its pore structure, including pore surface area, porosity and pore size distribution. Gullett and Bruce [17] investigated the sulfation behavior of CaO experiencing different sintering durations, and found that although sintering caused the coalescence of pores smaller than 7 nm and reduced pore surface area by a half, the sulfation behavior was not influenced significantly, which indicates that pores smaller than 7 nm are not crucial for the sulfation behavior of CaO. Ghosh-Dastidar et al. [18] found that the internal pore structures have a determining effect on the initial reactivity and the final utilization of CaO, but a high pore surface area cannot ensure a high sulfation reactivity and conversion. If the CaO particles contain an abundance of small pores, the sulfation reaction of the particle will cease prematurely because small pores are very susceptible to pore blockage and plugging. Interestingly, the study of Mahuli et al. [19] suggested that to improve the sulfation performance of CaO, not only the total pore surface and pore volume, but also the proportion of pores in the size range of 5–20 nm should be increased.

From the description above, in most of the studies, the calcination of limestone was carried out in $N_2$ or air, and then sulfation of the calcined CaO was studied. What is interesting and somewhat surprising is that few studies considered the influence of $SO_2$ on calcination of limestone. Under CFB conditions, limestone is calcined in flue gas produced by coal firing. In this case, there will be hundreds or thousands of ppm $SO_2$ in the flue gas. Therefore, a reasonable speculation is that the $SO_2$ will react simultaneously with a calcining limestone particle according to reaction (2). Hence, $CaSO_4$ will form in the particle, and the calcination of the particle will be affected by the formed $CaSO_4$ accordingly. Usually the decomposition of a limestone particle will proceed from the particle surface to the interior. Pores will form in the CaO layer, and serve as the diffusion path for $CO_2$. When sulfation takes place in the CaO layer, the $CaSO_4$ formed will fill and narrow the pores, increase the $CO_2$ transfer resistance, and consequently slow down the calcination reaction. There are several reasons why one should consider this hypothesis.