



Mechanisms of direct and in-direct sulfation of limestone



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HIGHLIGHTS

- SO₂ absorption area of direct sulfation was different from the indirect sulfation.
- The grain model can be applied to the indirect sulfation.
- The shrinking unreacted core model can be applied to the direct sulfation.
- The kinetic parameters of the reaction models were obtained from experimental data.
- The diffusion mechanism was considered both gas phase and solid-state diffusion.

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ABSTRACT

The general desulfurization process referred to as “indirect sulfation” takes place via a two-step process. Calcination makes limestone decompose to calcium oxide (CaO), and then SO₂ molecules are adsorbed onto the calcined limestone. However, if the CO₂ partial pressure in the system is higher than the equilibrium CO₂ pressure over the limestone, an adsorption reaction between limestone and SO₂ molecules can take place directly in the uncalcined state. This one-step process, called “direct sulfation,” can apply to desulfurization in pressurized fluid-bed combustion (PFBC) or an oxy-fuel combustion system capturing CO₂. Limestone samples were reacted in a TGA apparatus, and the degrees of sulfation were measured under 100% air conditions for indirect sulfation and 80% CO₂/20% O₂ conditions for direct sulfation to compare the mechanisms and kinetics of the two sulfation processes. SEM images of sulfated particles and EDS analyses showed that the gas diffusion of indirect sulfation takes place readily through macro-pores between the grains at a low conversion rate, and SO₂ adsorption occurs over the interior of the limestone particles, whereas SO₂ adsorption in direct sulfation takes place at the reaction interface, and the product (CaSO₄) layer permeates into the interior from the surface of the limestone particles as direct sulfation proceeds. Thus, the grain model and the shrinking unreacted core model are applicable to describing the kinetics of indirect and direct sulfation, respectively. These model predictions agreed with experimental data, and the kinetic parameters obtained from experiments are consistent with the mechanisms. Furthermore, the high activation energy of the diffusion of direct sulfation and indirect sulfation with high conversion indicate that the diffusion mechanisms in the particles in direct sulfation and indirect sulfation at high conversion are both gas diffusion in pores and solid-state diffusion. These results may contribute to understanding why the characteristics of direct sulfation differ from those of indirect sulfation under certain conditions.

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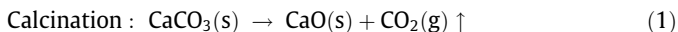
1. Introduction

In recent years, with growing concerns about environmental issues, various exhaust gas regulations have been strengthened, so that the sulfation process of limestone has been considered to reduce emissions of SO₂ from industrial facilities, such as coal

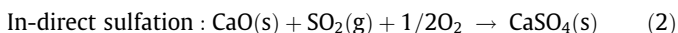
power plants, cement plants, and steel mills. Existing industrial facilities have generally disposed of SO₂ using flue gas desulfurization (FGD) systems, which operate with wet scrubbing using a slurry of limestone or spray-dry scrubbing. In spray-dry scrubbing, the desulfurization process with limestone takes place through a two-step process. First, the calcination of limestone occurs in a high-temperature furnace under low CO₂ partial pressures. The calcination process makes limestone decompose to calcium oxide (CaO), as expressed by the following equation.

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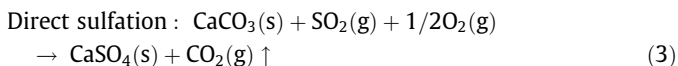
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After the calcination, SO₂ molecules are adsorbed onto pores of the calcined limestone (CaO), as expressed by the following equation.



This two-step process is referred to as “indirect sulfation.” However, if the CO₂ partial pressure in the system is higher than the equilibrium CO₂ pressure over the limestone, it prevents the calcination (decomposition) of calcium carbonate [1]. Then, the adsorption reaction between limestone and SO₂ takes place directly in the uncalcined state, as expressed by the following overall reaction.



This one-step process is called “direct sulfation.”

This direct sulfation of limestone has been shown to occur in the desulfurization process during pressurized fluid-bed combustion (PFBC) or with SO₂ absorption at the cyclone preheater stage in cement production. In these processes, because the operating pressure is very high, the partial pressure of CO₂ is enough to prevent calcination of the limestone. Moreover, in addition to these processes, the desulfurization process during oxy-fuel combustion is relevant to direct sulfation. The oxy-fuel combustion system, which enables easy CO₂ recovery, has recently been introduced as a promising combustion system in the power plant industry as regulations about the emission of greenhouse gases have become more severe. Thus, it has been noted as a useful technology for capturing CO₂ to remove CO₂ from emissions. In oxy-fuel combustion, O₂ is separated from air in an air separation unit (ASU) and is used as an oxidizer, instead of air, in the furnace. Because materials cannot withstand the resulting high flame temperature in the furnace, the temperature in the furnace has to be reduced by flue gas recirculation (FGR). This causes the atmosphere in the furnace to be composed primarily of CO₂, with a small amount of O₂, so the partial pressure of CO₂ is sufficiently high to prevent limestone calcination [2]. The equilibrium CO₂ pressure over the limestone that occurs in calcination can be described by the following equation [3]:

$$\log_{10} P_{\text{CO}_2}^e (\text{atm}) = -\frac{8308}{T(\text{K})} + 7.079 \quad (4)$$

According to this equation, calcination of limestone begins at 700 °C under ‘commercial atmospheric conditions,’ but it starts to react at more than 900 °C under oxy-fuel conditions (90% CO₂ + 10% O₂). Thus, direct sulfation should be applicable to desulfurization under oxy-fuel combustion conditions.

Various papers have discussed the mechanisms of direct sulfation of limestone in comparison with indirect sulfation. Ulerich [4] suggested that slower diffusion of the CO₂ formed by decomposing limestone particles caused the lower sulfation rate because CO₂ concentrations were higher. Tetard [5] observed that the solid-state mobility of limestone was affected by the CO₂ partial pressure. Liu [6] explained that the degree of direct sulfation was higher than that of indirect sulfation as the reaction time increased, although the indirect sulfation rate was higher than the direct sulfation rate at lower conversions because sintering was greatly mitigated during direct sulfation of limestone. Snow [7] observed that the product layer formed by direct sulfation of limestone was porous, whereas the sulfate layer formed from calcined stone was less porous due to generation of CO₂ at the unreacted surface of limestone during direct sulfation. Hu [8] suggested that the direct sulfation of limestone involved five general steps: gas-film diffusion, pore diffusion, the chemical reaction, solid-state diffusion, and nucleation and crystal grain growth of the solid

product. Thus, direct sulfation is usually under mixed control, partly by the chemical reaction and partly by solid-state diffusion, at low temperatures and low conversions.

Various models to describe the kinetics of the sulfation reaction have been discussed in connection with simulating the behavior of limestone in the sulfation process. The shrinking unreacted core model [9,10] is the most commonly used model for limestone sulfation. Many researchers [6–7,11–14] have described the kinetics of sulfation by appealing to the shrinking unreacted core model, which assumes a clear interface between the unreacted core and the product layer during gas–solid reactions of the sorbent particles. The changing grain size model was developed to describe the kinetics of the sulfation process by Garcia-Labiano [15]. It assumes that a particle is composed of an assembly of small grains, and as the reaction proceeds, the grain size grows. Many researchers [16,17] have applied the changing grain size model to explain the kinetics of the sulfation process. The random pore model was developed by Bhatia [18]. Pores are created randomly on the inside of the particles in this model. Spartinos [19] approached the description of the sulfation process using the parallel pore model, which is similar to the random pore model, except for the placement of the pores.

The kinetics of the sulfation process of limestone particles has been studied by various researchers using these models. Simons [20] explained that SO₂ and O₂ diffuse through the pores of the limestone particles and that the sulfation reaction is controlled by the chemical reaction among SO₂, O₂, and the surfaces of the individual grains of calcined limestone (CaO). The reaction rate for the sulfation process of small particles ($d_p < 50 \mu\text{m}$) was reported to be controlled by the chemical reaction, with an activation energy of <100 kJ/mol [7,12], but for larger particles ($d_p > 50 \mu\text{m}$), the reaction rate for the sulfation process was found to be controlled by product layer diffusion, with activation energy of >100 kJ/mol [21]. Hu [8,22] explained that the sulfation process was most likely under mixed control, by the chemical reaction and solid-state diffusion, at low temperatures and low conversions, but that as the degree of conversion increased, solid-state diffusion became the dominant control mechanism. Chen [23] also explained that direct sulfation was controlled by solid-ion diffusion at the inner layer, although gas-phase diffusion takes place in the pores of the outer later. These models describing the kinetics of the sulfation process of limestone have been analyzed indirectly from empirical data such as the degree of sulfation, the rate of conversion, and the pore size of the particles. Thus, although there are various theories of the mechanisms and kinetics of the indirect and direct sulfation processes, the need for further clear evidence to explain them fully remains.

In this work, thermogravimetric analysis (TGA) experiments were conducted to explore differences in the mechanisms of indirect and direct sulfation. Models for describing the kinetics of the direct and indirect sulfation processes of limestone were determined through analysis of the surface and the inner morphology of the reacted limestone samples, observed by scanning electron microscopy (SEM), and the chemical composition of their interior parts, analyzed by energy-dispersive X-ray spectroscopy (EDS). The kinetic parameters of the models were determined by measuring the rates of the direct and indirect sulfation of limestone in the temperature range 700–850 °C.

2. Experimental method

2.1. Thermogravimetric analysis

The experiments were performed by TGA (TG 209 F3, Netzsch). Two carrier gases were supplied to the experimental set-up to

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