

Direct Desulfurization and Re-carbonation of Limestones under Oxy-Circulating Fluidized Bed Combustion Conditions

Ye Bin Kim¹, You Ra Gwak¹, See Hoon Lee^{1*}

¹ Department of Resources and Energy Engineering, Chonbuk National university, Jeonju, Chonbuk, 54896, Korea

*Corresponding author: donald@jbnu.ac.kr

Highlights

- The limestones behaviors under simulated Oxy-CFBC conditions were investigated in TGA.
- Direct desulfurization and re-carbonation were studied under CO₂ concentration(60-100%).
- Reaction models are proposed and evaluated to predict the behavior of limestones.

1. Introduction

In recent years, oxygen firing or oxygen-blown combustion technologies have been widely considered as a suitable and economical solution for addressing global warming due to an increase of atmospheric CO₂ concentration. With these technologies, the CO₂ concentration in the flue gas may be up to over 90%. Therefore, an easy CO₂ capture and storage becomes possible[1].

Compared with oxy-pulverized combustion(Oxy-PC), oxy-circulating fluidized bed combustion(Oxy-CFBC) may be better choice for CO₂ capture because of lower combustion temperature, widely adaptable fuels, in situ sulfur capture, and lower NO_x emissions[2]. Because of recirculating a part of the generated flue gas, high concentration of CO₂ could be recovered and the concentrations of SO₂ and CO₂ might be different from the conditions of air-blown CFBC. Therefore, the limestone for desulfurization in CFBC can be surrounded by higher CO₂ concentration during Oxy-CFBC operation.

As shown in Fig. 1, various reactions with limestone might happen during Oxy-CFBC operation [3, 4]. However, studies or experimental results for direct desulfurization and re-carbonization under Oxy-CFBC conditions might be insufficient. In this study, the limestone sulfation behavior and re-carbonization under Oxy-CFBC conditions was investigated by using thermogravimetric analyzers (TGA). Also, reaction models to predict the behavior of limestones with various CaO fractions were proposed.

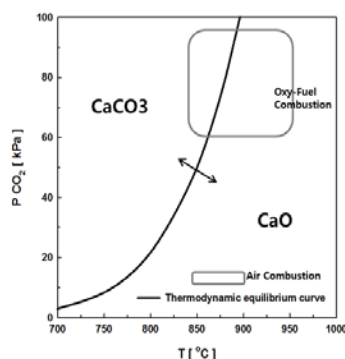


Figure 1. Equilibrium CO₂ partial pressure over limestone.

2. Methods

Direct desulfurization reactions of 4 different limestone samples (CaO fraction: 40-55%) were measured by using a TGA (SETSYS), which has been commonly used for comparing and evaluating reaction kinetics. Also, the re-carbonation characteristics of CaO samples calcined 4 different limestones were measured using a different TGA(TGA-N1000). Direct desulfurization of the limestone was carried out by setting the flow

rate at 40cc/min, and the weight change by the reaction was analyzed using an electronic balance with a sensitivity of 10^{-5} g. The reaction gas was injected to the top and discharged to the bottom. The sample was fixed on an alumina basket inside the reactor and the reaction proceeded. Direct desulfurization of all samples was conducted at 600-950°C, 2750 or 5000ppm SO₂-CO₂ balance, 60-95% CO₂, and 5-40% O₂. To investigate re-carbonization of CaO, limestone samples were calcined at 850°C in a 200mL/min flow of Air. The re-carbonization was conducted at 600-870°C, under pure CO₂ condition after heating with N₂.

3. Results and discussion

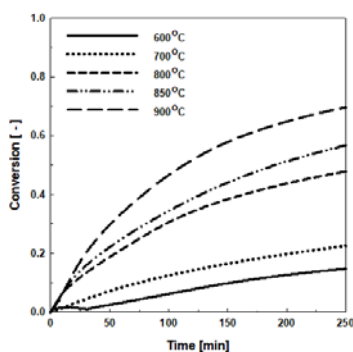


Figure 2. Conversion of limestone S1 according to CO₂ 60% (direct desulfurization)

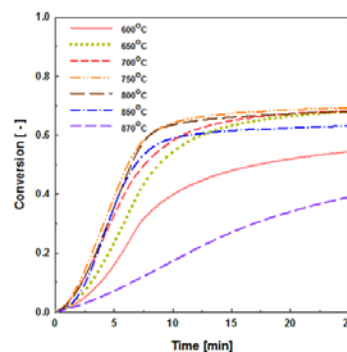


Figure 3. Conversion of limestone S1 (re-carbonation)

In the desulfurization experiment, the conversion of direct desulfurization reaction increases as the temperature increases. It can be seen that the desulfurization conversion rate continues to increase even after 3 hours depending on the limestone. In addition, regardless of the concentration of CO₂, the desulfurization conversion constantly increases as the temperature increases. Compared to indirect desulfurization, the conversion continuously increased in the direct desulfurization experiments. As shown in Fig 3, the re-carbonation reaction was also decreased as the temperature was increased more than 850°C.

4. Conclusions

The direct desulfurization mechanism was studied with temperature ranging from 600°C to 950°C at 60-95% of CO₂ concentration. As the temperature increased, the calcium conversion increased up to 900°C. In order to predict the behavior of limestone, the data derived from the experiments were analyzed and used for direct desulfurization reaction models (SCM, VRM, MVRM and Random Pore). Also, re-carbonization reaction models were proposed.

References

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Keywords

Oxy-fuel combustion, circulating fluidized bed combustion, limestone, desulfurization