



A study on the calcination and sulphation behaviour of limestone during oxy-fuel combustion

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HIGHLIGHTS

- ▶ The inhibition of CO₂ on limestone calcination can be compensated by coal flame.
- ▶ Direct sulphation was pronounced at high SO₂ concentration and excess calcium.
- ▶ The interaction between Si/Al and limestone was favoured in oxy-fuel mode.

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ABSTRACT

The mechanisms governing the behaviour of limestone for in-furnace desulphurisation during oxy-fuel combustion have been investigated in this paper. Apart from the use of pure limestone, the mixtures of limestone with a brown coal (i.e., lignite) at different mass ratios have also been examined to address the influence of ash on the behaviour of limestone. The combustion experiments were conducted in a drop-tube furnace at a furnace temperature of 1273 K and a reactor length of 1200 mm for a nominal particle residence time of approximately 1.0 s. Pure air and an O₂/CO₂ mixture at a volume ratio of 27:73 were tested. SO₂ at a concentration of 1000 ppm was also doped into these two gases to examine its competition with Si and Al in the ash on the interaction with limestone. A high CO₂ partial pressure has been confirmed to slow down the calcination of limestone in O₂/CO₂. However, mixing limestone with coal enhanced the limestone calcination by increasing the particle temperature through radiative heat transfer from flame. With a large quantity of limestone such as the 18% tested here, direct sulphation is a major route contributing to sulphur capture during oxy-fuel combustion. The importance of direct sulphation is exceeded by indirect sulphation via an initial calcination of limestone when medium and low quantities of limestone are added to coal. The Si and Al in coal undermine the calcination and sulphation of limestone in O₂/CO₂ because of the preferential formation of Ca aluminosilicate eutectics. These eutectics tend to melt and deposit on the unreacted limestone surface, thus providing extra resistance to the diffusion of gas through the limestone particles. Increase of SO₂ content in flue gas favours the indirect sulphation of calcium over the interaction of calcium with ash, thereby increasing the extent of desulphurisation during oxy-fuel combustion.

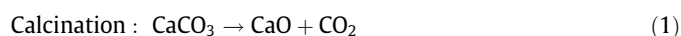
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1. Introduction

Oxy-fuel combustion is a promising technology for coal-fired power plants to quickly adapt to existing power stations to mitigate the greenhouse gas emissions from coal combustion. During the typical oxy-fuel combustion process, the flue gas is recirculated to mix with high-purity oxygen as a replacement for combustion air. The resulting CO₂ concentration in the flue gas is expected to reach up to 95%. However, because a large portion of the flue gas

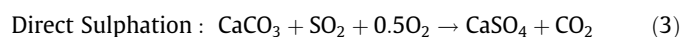
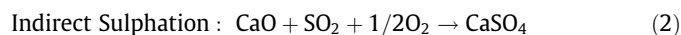
is recycled, the gaseous impurities such as SO₂/SO₃ within that flue gas can gradually accumulate in a furnace. This accumulation, in turn, potentially causes extra fouling and tube corrosion problems through the deposition of sulphates. An efficient capture of SO₂ for flue gas cleanup is pivotal for eliminating these potential problems during oxy-fuel combustion.

Capture of SO₂ through in-furnace injection of limestone is one promising option for flue gas cleanup. In conventional air combustion, the sulphur removal with limestone involves two consecutive steps: calcination of limestone and sulphation of lime (calcium oxide), according to reactions (1) and (2) as follows:



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The calcination of CaCO_3 by reaction (1) is affected by two factors, CO_2 partial pressure and limestone particle temperature. The CO_2 partial pressure plays a negative role in CaCO_3 decomposition. However, an increase in particle temperature through radiative heat transfer from the coal flame may offset the influence of the CO_2 partial pressure. The direct sulphation of limestone according to reaction (3) is also relatively important for sulphur capture, particularly during oxy-fuel combustion. A general understanding of this reaction has yet to be demonstrated in the literature. Liu and his co-workers [1] concluded that, as the sintering of limestone in CO_2 is substantially decreased, the direct sulphation of limestone exhibits a rate comparable to the indirect sulphation in reaction (2). Our previous results also confirmed the large potential for the occurrence of reaction (3) in O_2/CO_2 under certain conditions [2]. Fuertes et al. [3] and Snow et al. [4] suggested that the direct sulphation reaction is chemically controlled. By contrast, Lisa and Hupa [5] hypothesised that gas diffusion is the controlling step limiting the extent of the direct sulphation of limestone. Some researchers also proposed comparable significance for reaction control and a diffusivity limit [6,7]. All these studies have not taken the presence of Si and Al in the ash into account. The Si and Al in coal are important because of their interaction with limestone at high temperatures. This high-temperature reaction favours the formation of molten eutectics on the fireside and, hence, inhibits the efficiency of the in-furnace desulphurisation during air combustion [8].

The present study aims to address these knowledge gaps to clarify the transformation behaviour of CaCO_3 during oxy-fuel combustion. The interaction of coal-bound metals with limestone has been elucidated in detail, through the combustion of limestone mixed with lignite at different mass ratios. The lignite used was Victorian brown coal with an abundance of organically bound metals. The combustion of this lignite at high temperatures was expected to deliver an abundance of fine and even ultra-fine ash particles, which can attack limestone through random collision. The doping of 1000 ppm SO_2 into the flue gas was also performed to mimic the gradual accumulation of this impurity gas in an oxy-firing furnace. The solid products from all the combustion tests were subjected to a variety of advanced analytical techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD) and computer-controlled SEM (CCSEM) for the analysis of both the bulk properties of the overall ash and the determination of the size-dependent characteristics of individual particles. Mathematical modelling through a shrinking core model was also conducted to clarify the resistance of the ash layer against the diffusion of gases during the calcination and sulphation of limestone.

2. Experiment

A commercial reagent-grade limestone with an average particle size of 21 μm was tested. The coal sample used to mix with the limestone was an air-dried brown coal collected from Victoria, Australia, shown in Table 1. The size of the coal particles ranged from 106 to 153 μm , and the sulphur and ash (determined by high temperature ashing in a muffle furnace at 873 K) accounted for 0.9 wt.% and 2.24 wt.%, respectively. The volatile matter accounted for more than half of the weight of the dried coal. The volatile matter thus formed a burning volatile cloud in the oxidising atmosphere [9].

All the combustion experiments were performed in a laboratory-scale drop tube furnace (DTF). A schematic diagram and a

Table 1
Properties of the brown coal.

<i>Proximate analysis, air-dried, wt.%</i>	
Fixed carbon (FC)	42.1
Volatile matter (VM)	42.4
Ash	2.24
Moisture	13
<i>Ultimate analysis, daf, wt.%</i>	
C	69.3
H	6.7
N	0.6
O by difference)	22.5
S	0.9
<i>Ash compositions, wt.%</i>	
SiO_2	41.2
Al_2O_3	25.4
SO_3	10.1
MgO	6.13
TiO_2	7.03
Na_2O	5.00
Fe_2O_3	2.68
CaO	1.68
K_2O	0.297
P_2O_5	0.202

description of the operating procedure have been provided in detail elsewhere [10]. The furnace temperature was fixed at 1273 K. Pure limestone or a coal-limestone mixture at a feed rate of 0.5 g/min was fed into the furnace by 1 L/min of primary gas (cold). A pre-heated secondary gas at 9 L/min was also fed into the reactor to assist coal combustion. Two major bulk gases, air and 27% $\text{O}_2/73\% \text{CO}_2$, were tested because they match each other in terms of flame propagation speed and burning coal particle temperature [9]. Three percentages of limestone (18%, 5% and 1%) in the limestone-coal mixtures were tested. The corresponding Ca/S molar ratio and the mass ratio of limestone to ash are tabulated in Table 2. The different percentages of limestone added to the coal were supposed to address the effect of ash on the performance of limestone as the ratio of limestone to ash is changed. In addition, an extra SO_2 content of 1000 ppm was doped into either air or 27% $\text{O}_2/73\% \text{CO}_2$ and was further examined. Two reactor lengths (1200 mm and 600 mm) provided a particle residence time of approximately 1 s and 0.6 s in the furnace. The solid products from each run, hereafter termed ash, were separated into coarse ($>5.0 \mu\text{m}$) and fine fractions ($\leq 5.0 \mu\text{m}$) in this study. No less than three repetitions were performed for each set of conditions to obtain satisfactory accuracy for ash yield and calcium recovery throughout this study.

The unreacted CaCO_3 fraction in a solid ash sample was quantified by heating in a temperature-programmed thermogravimetric analyser (TGA, DTG-60/60H, Shimadzu) at 10 K/min. The drop from room temperature to a temperature range of 873–1073 K was considered to be the decomposition process of CaCO_3 , as detailed in Fig. S1 in the Supporting information (SI).

The elemental components of the ash products were quantified using X-ray fluorescence (XRF). The sulphur content as determined

Table 2
Experimental conditions tested and the corresponding Ca/S molar ratios and limestone-to-ash mass ratios.

Limestone percentage (%)	Extra 1000 ppm SO_2	Ca/S (Molar)	Limestone/Ash (Mass)
18	No	16.0	8.0
18	Yes	3.8	8.0
5	No	4.4	2.2
5	Yes	1.1	2.2
1	No	0.9	0.4
1	Yes	0.2	0.4

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