

SO₂ retention in Oxy-Coal fluidized bed combustors and its influence on pollutant gases

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OBJECTIVES AND NOVELTY

Oxy-fuel combustion is one of the Carbon Capture and Storage (CCS) technological options which consists of burning the fuel with a mix of pure oxygen and recycled flue gas which is mainly composed of CO₂. Therefore, the CO₂ concentration in the flue gas may be enriched up to 95% to be subsequently transported and stored. Many of the current researches are related to oxy-fuel pulverized coal (PC) combustion. However, oxy-fuel combustion of coal in circulating fluidized bed (CFB) combustors has received relatively little attention. One of the main advantages of this technology compared to PC boilers is the possibility of performing the in situ desulfurization process via Ca-based sorbents added into the combustor. According to the equilibrium curve of CaCO₃ calcination (see Figure 1), the desulfurization process with Ca-based sorbents is highly dependent on the temperature and concentration of CO₂. At typical air fluidized bed (FB) combustion conditions, the sorbent always calcines (R1) and thus the sulfation of the CaO, so-called indirect sulfation, takes place (R2). However, under oxy-fuel combustion, the sorbent can be surrounded by CO₂ concentrations ranging from 60 to 90 % and thus sulfur retention can be produced under indirect (R2) or direct sulfation (R3). Therefore, the behavior of the sorbent in oxy fuel mode has yet to be elucidated.

The present work aims to analyze the effect of the main oxy-fuel FB operating variables (O₂/CO₂ feeding ratio, coal rank, type and particle size of the sorbent, etc.) on the desulfurization process via Ca-based sorbent fed into the combustor. To reach this objective, four Ca-based sorbents (three limestones

and one dolomite) and three coals ranging from lignite to anthracite have been used. Moreover, a detailed study of the influence of the recycled flue gas (typical in the oxy fuel combustion process) in the emission of pollutant gases (NO_x and Hg) in the outlet gas stream has been carried out.

RESULTS

Firstly, an analysis of the chemical and physical properties of the Ca-based sorbent was carried out. Limestones presented a high CaCO₃ content, ranging from 92 to 97 %, whereas the dolomite almost contained the same percentage of both CaCO₃ and MgCO₃, 52.5 and 40.5 % respectively. In addition the calcined sorbents were observed to present higher porosity than the raw sorbent since the CaO molar volume is higher than that of CaCO₃. The ultimate and immediate analyses of the coals were also determined where it is worth mentioning their different sulfur content: lignite = 5.17%, bituminous coal = 0.77 % and anthracite = 1.52 %.

Experimental tests in a thermogravimetric analyzer (TGA) and in a batch FB were later performed to analyze the reactivity of the sorbents. It was observed that the sulfation reaction was carried out in two steps, the former being faster than the latter. The dolomite exhibited higher sulfation conversions (X_s) than the limestone. The highest sulfation conversions were reached at calcining conditions and an optimum temperature was found to be around 900-925 °C. Regarding the CO₂ concentration, once the calcining or non calcining conditions were defined, this variable hardly had any influence on sulfation conversion. Based on these results, a sulfation kinetic model operating under calcining conditions was developed

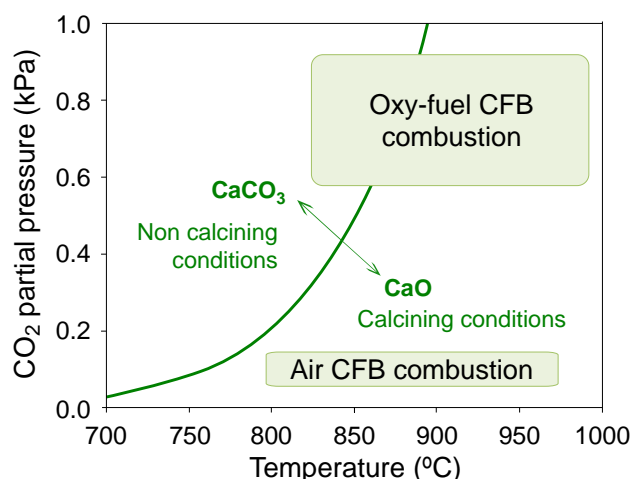
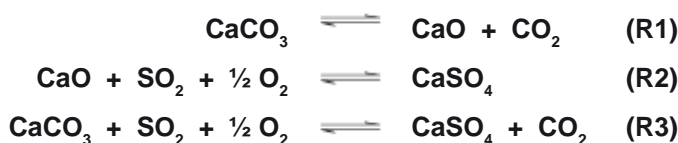


Figure 1. Thermodynamic equilibrium curve of CaCO₃ calcination

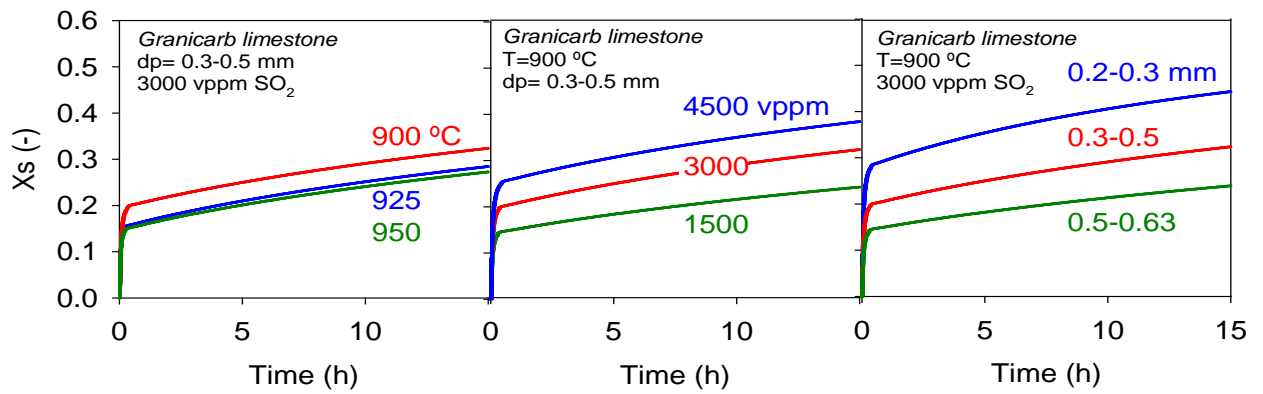


Figure 2. Sulfation conversion curves predicted by the sulfation kinetic model developed.

taking into account both steps (see Figure 2). The first one was controlled by the diffusion of the reactant gas through the porous system of the sorbent particle and the second one by the diffusion of the reactant gas through the product layer of the particle according to Shrinking Core Model (SCR).

Experimental tests in a Bubbling Fluidized Bed (BFB) combustor (3 kW_{th}) with a continuous sorbent/coal feeding were carried out. The effect of the O₂/CO₂ feeding ratio, coal rank and type and particle size of the sorbent on sulfur retention (SR) was analyzed. Coinciding with the results obtained in TGA and batch FB, an optimum temperature from the point of view of the sulfur retention around 900- 925 °C was found. Besides, it was observed that the higher the sulfur content of the coal, the higher the sulfur retention. Regarding the type and particle size of the sorbent, the highest sulfur retention values were achieved working with the dolomite and with the smallest particle sizes. Moreover, an increase in the O₂ concentration feeding produced a slight increase in the sulfur retention. Concerning the recycled flue gas, the SO₂ recirculation was observed to produce an increase in sulfur retention (see Figure 3) due to the increase of SO₂ concentration inside the boiler which enhances the sorbent sulfation process. Neither NO nor H₂O affected the sulfur retention process. However, an important NO reduction, mainly to N₂, at the outlet gas stream after steam recirculation was observed. Likewise, when the NO recirculation was carried out, a reduction of the recycled NO to N₂ nearly 70 % was also detected. Moreover, it was observed that most of the Hg was retained by the particle matter (sorbent) and the SO₂ inhibited the oxidation reaction from Hg(0) to Hg(II).

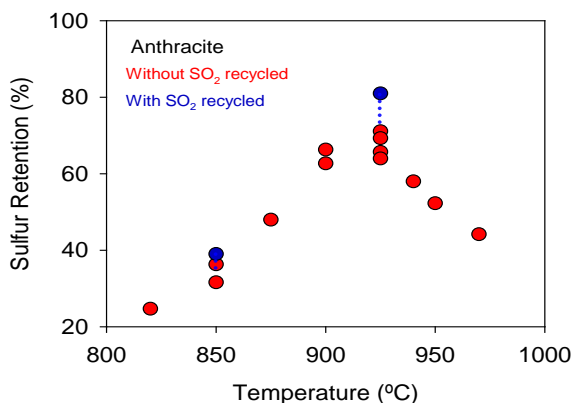


Figure 3. Effect SO₂ recirculation on sulfur retention. Granicarb, O₂/CO₂ = 35/65, Ca/S = 3

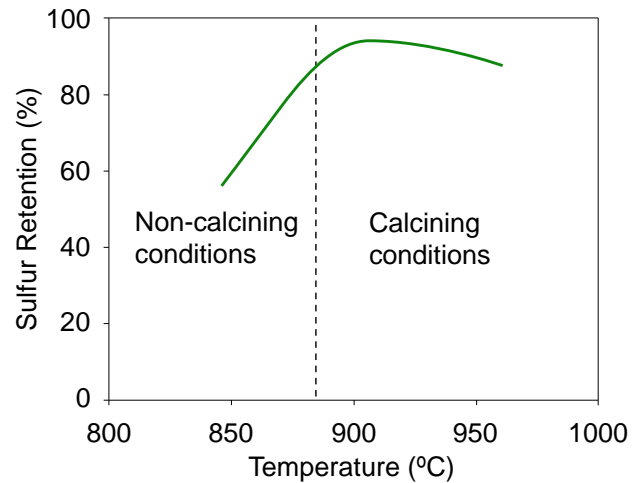


Figure 4. Simulation of the effect of the temperature on sulfur retention.

Subsequently, an air CFB combustion model (1.5D) previously designed and validated by the research group was adapted to oxy-fuel combustion conditions. For this purpose, the recycled flue gas stream and the sulfation kinetic model developed in this work were incorporated in the CFB model. The model consisted of a hydrodynamic sub-model, a coal combustion sub-model and a sulfur retention sub-model. The simulation of this CFB model has been able to predict the longitudinal profiles of the different gaseous products (O₂, CO, CO₂, H₂O and SO₂) along the boiler, the combustion efficiency and the sulfur retention reached at different operating conditions. The effects of the main operating variables were simulated in order to optimize the sulfur retention process.

Coal combustion efficiency around 96-97 % was achieved for the three coals used. It was observed that an increase in the O₂ concentration feeding produced a slight increase in the sulfur retention and an optimum temperature with respect to sulfur retention nearly 900-925 °C was found (see Figure 4). Likewise, an increase in Ca/S molar ratio caused an increase in the sulfur retention. Analyzing the reactivity of the sorbent, it was found that the influence of the diffusional coefficient of the second step of the sulfation reaction was more relevant than that of the first step, corroborating the results reported by other authors about the importance of the residual activity of the sorbent. Eventually, the possibility of using or not using the desulfurization unit in the recycled flue gas was evaluated. The sulfur retention without desulfurization unit was higher than that with

the desulfurization unit although the SO₂ emissions were also higher. In both cases, Ca/S molar ratio around 2.5 was needed to fulfil the requirement of CO₂ transport.

CONCLUSIONS

A comprehensive study analyzing the effect of the main variables on SO₂ retention process in oxy-FB combustors has been performed by means of experimental tests in a BFB combustor and CFB simulation.

An optimum temperature with respect to sulfur retention corresponding to calcining conditions was found to be around 900-925 °C. The dolomite reached a higher sulfation conversion than the limestones. Moreover, it was observed that the sorbent sulfation reaction was carried out in two steps, the former being faster than the latter.

Regarding the results obtained in a BFB combustor, the coal rank, sorbent particle size and SO₂ recirculation were the main variables affecting SO₂ retention process. The steam and NO recirculation were the main variables affecting NO emissions at the outlet gas stream. Most of the Hg was retained by the particle matter (sorbent) and the SO₂ inhibited the oxidation reaction from Hg(0) to Hg(II).

Based on simulation results of the oxy-CFB model (1.5D), operating in calcining conditions at 900-925 °C, Ca/S around 2.5 and sorbent particle size close to 0.15 mm was needed to fulfil the requirement of CO₂ transport.

RELATED PUBLICATIONS

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