INVESTIGATION OF SO₂ CAPTURE IN A CIRCULATING FLUIDIZED BED
CARBONATOR OF A Ca-LOOPING CYCLE

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ABSTRACT

Calcium looping is a post-combustion CO₂ capture technology that uses CaO as a regenerable solid sorbent. One potential advantage of this technology is that it allows flue gases to be treated with SO₂, avoiding the need for a costly desulfurization step. In this work, we study the desulfurization capacity of a CFB carbonator reactor in a 30 kW_{th} pilot plant that has been used to test CO₂ and SO₂ co-capture. A simple reactor model is applied to analyze the experimental results obtained and to study the effect of the main variables involved in the process: i.e. the circulation rates of solids and the inventory of active material in the CFB reactor. The results obtained have shown that SO₂ capture efficiencies above 0.95 can be achieved in a CFB carbonator even when using a low inventory of active material in the bed. Extreme

desulfurization (SO_2 emissions below 5-10 ppmv) is thought to be achievable in large scale CFB carbonators designed to capture CO_2 with CaO .

INTRODUCTION

Calcium looping is an emerging post-combustion CO_2 capture technology that uses CaO as a regenerable solid sorbent. In this system, CO_2 from the combustion flue gas of a power plant is captured by using CaO as sorbent in a circulating fluidized bed (CFB) carbonator operating between 600-700 °C. The stream of partially carbonated solids leaving the carbonator is directed to the CFB calciner, where the solids are calcined by burning coal under oxy-fuel conditions at temperatures above 900 °C, allowing the release of the CO_2 captured from the power plant and the regeneration of the sorbent (CaO). The CFB reactors used in Ca looping operate with solid materials (mainly CaO particles and ashes) and key operating conditions (gas velocities and solid circulation rates) very similar to those present in large scale CFB combustors. This advantage explains the rapid development of this technology in recent years from small laboratory scale pilot plants^{1,2,3,4,5,6} to larger pilot plants with a scale of 200 kWth⁷ and 1 MWth's^{8,9,10}.

Other features of the process are that the heat supplied to the calciner can be recovered from different high temperatures sources, thus ensuring an efficient heat integration through the entire power plant and a lower energy penalty^{11,12,13,14,15,16}. Another important aspect of CaL compared to other post-combustion CO_2 capture technologies (e.g. amine systems) is that the flue gas treated can contain a certain amount of SO_2 since CaO from calcined limestones is used in many commercial scale power plants¹⁷. Several works on sulfation phenomena in CaL systems have been published although these focus mainly on the effect of SO_2 on CO_2 carrying capacity during cycling^{18,19,20,21,22,23,24,25}. These studies have referred to the negative impact upon SO_2 on

sorbent capacity and the increasing decay of CO₂ carrying capacity of the sorbent during cycling due to the irreversible sulfation reaction of CaO. Some researchers^{18,20,23} have shown that the SO₂ absorption capacity of cycled CaO is higher than that of the fresh calcined limestone due to fact that the sintering process causes the pores to open. These researchers have also suggested the idea of using the spent sorbent from calcium looping as feedstock material for SO₂ retention in CFB boilers during coal combustion. However, it should be noted that a simple mass balance on the continuous operation of Ca looping²⁶ reveals that the large makeup flows of limestone required to purge the ash and maintain sorbent activity results in very low average particle sulfation values (sulfation conversions below 5 mol%). In any case, the loss of activity due to the irreversible reaction between CaO and SO₂ can be compensated for by adding fresh sorbent due to the low cost of limestone and by taking advantage of synergy with the cement industry^{27,28}. Other aspect of the presence of SO₂ in Ca-looping is the effect on sorbent attrition. Different trends have been reported in the literature. Some authors²⁹ have found that the presence of SO₂ can reduce the attrition of the sorbent during CO₂ capture in CFB reactor. However, a recent work carried out by Coppola *et al.*³⁰ has reported that SO₂ has little impact on sorbent attrition during CO₂ capture in a fluidized bed reactor.

The fact that Ca looping allows flue gases to be treated with SO₂ offers the possibility of avoiding the desulfurization step and removing the SO₂ during CO₂ capture process. However, to our knowledge no experimental has demonstrated the ability of a CFB carbonator to retain SO₂ under the typical conditions expected of a carbonator in a calcium looping system. The aim of this work is to study the desulfurization capacity of a CFB carbonator in a small pilot plant composed of two interconnected fluidized beds during CO₂ capture operating in continuous mode (i.e. continuous circulation of solid between the calciner and carbonator). A simple reactor

model is proposed to analyze the experimental results obtained and to study the effect of the main variables involved in the process.

EXPERIMENTAL

The tests shown in this work were carried out in the 30-kW pilot plant at INCAR-CSIC which has been described elsewhere ⁵. Figure 1 outlines the Ca-looping process and the main variables analyzed during an experimental campaign to test SO₂ capture in the carbonator. This facility consists of two interconnected CFB reactors: a carbonator 6.5 m in height and a calciner 6.0 m in height. Both reactors have an internal diameter of 0.1 m. The facility is electrically heated by independently controlled ovens. Each reactor is equipped with a primary cyclone which separates the solids and flue gases leaving the risers. In order to close the pressure balance and to return the solids to the riser, each reactor is equipped with a loop seal which consists of a bubbling fluidized-bed aerated with air. A simulated flue gas is supplied to the carbonator by mixing air, CO₂ and SO₂ by means three mass flow controllers. For this study, the calciner was operated burning coal with air. The composition of the flue gas leaving both reactors was measured by two continuous gas analysers. The inventory of solids in each reactor was calculated from the pressure drop in the risers. During the tests samples of solids from the risers were taken using sampling ports. The conversion of CaO to CaCO₃ and CaSO₄ was calculated by determining the carbon and sulfur content of the samples of solids using a LECO CS 230. The samples were also tested in a TG equipment to determine their maximum CO₂ carrying capacity (X_{ave}).

Figure 1. Scheme and main variables in the calcium looping process for CO₂ capture incorporating SO₂ co-capture.

Compostilla limestone was used in all the experiments (main components of calcined limestone: 95.4 %_{w t} CaO, 2.6 %_{w t} Fe₂O₃, 0.8 %_{w t} MgO, 0.5 %_{w t} K₂O) the initial average size of the particles being 105 μm. The main input of sulfur into the system was the flue gas fed into the carbonator. A low ash and sulfur coal was used during the tests (71.0 % C, 4.4 % H, 0.2 % S, 3.9 % ash) to facilitate the analysis of SO₂ capture in the carbonator. The experimental procedure applied is similar to that described by Rodriguez et al.⁵. For each test an initial batch of 20 kg of limestone was used. The solids were calcined by burning coal in the carbonator and calciner. After this initial calcination, the coal fed into the carbonator was stopped to allow the

temperature to fall to a value between 600-700 °C. Once this temperature had been reached, synthetic flue gas was fed into the carbonator in order to start the co-capture test.

Table 1. Range of operation conditions and range of main parameters

Carbonator temperature (°C)		575-685
Carbonator superficial gas velocity (m s^{-1})		2.1-2.9
Inlet CO ₂ volume fraction		0.06-0.15
Inlet SO ₂ concentration (ppmv)		1300-6250
Inventory of solids in the carbonator (kg m^{-2})		20-255
Maximum CO ₂ carrying capacity of the solids		0.04-0.18
CO ₂ capture efficiency		0.10-0.50
SO ₂ capture efficiency		0.70-1.00

Table 1 resumes the main parameters involved in the carbonator reactor and the range of operating conditions. Initial tests showed that a high inventory of active solids in the carbonator (as needed for an efficient capture of CO₂⁵) leads to extremely high SO₂ capture efficiencies (close to 1). Since the information from these tests is of little use for model validation purposes or to elucidate the effect of the variables involved in the SO₂ capture process, most of the tests were carried out under experimental conditions that lead to SO₂ capture efficiencies well below 1, even though in these conditions, CO₂ capture efficiencies were unacceptably low. This was achieved by using an unrealistically high SO₂ concentration in the flue gas fed into the reactor and lower than usual inventories in the carbonator and lower solids circulation rates from the calciner.

Figure 2 shows an example of an experimental testing period of 40 minutes. The O_2 , CO_2 and SO_2 concentration at the exit of the carbonator are shown in the first graph. The second graph shows the inventory of solids in the carbonator and the reactor temperature. The carbonator temperature shown in the second graph of Figure 2 corresponds to the average value calculated from the temperatures measured at the bottom of the carbonator where the dense bed is located. The third graph shows the CO_2 and SO_2 capture efficiencies calculated from the gas composition measured at the exit of the carbonator reactor.

The experimental run illustrated in Figure 2 is divided into four periods with different SO_2 inlet concentrations and solids inventories of solids. During this experimental run, the total flow to the carbonator and the CO_2 molar fraction at the inlet was kept constant at 0.12. The SO_2 inlet concentration to the carbonator during the initial period (1) was kept at 1900 ppmv. The SO_2 capture efficiency during this period was around 0.98, since the SO_2 concentration at the exit of the carbonator was around 40 ppmv. After this period, the SO_2 inlet concentration was increased to 3800 ppmv. This increase in the inlet concentration led to an increase in the SO_2 concentration at the exit of the carbonator and a reduction in SO_2 capture efficiency to a value of around 0.95. During the 3rd period, the SO_2 inlet concentration to the carbonator was set to 1800 ppmv. A reduction in the SO_2 at the exit of the carbonator was observed at this point which stabilized to a value close to 60 ppmv. The SO_2 capture efficiency during this period was 0.97, slightly lower than during the initial period due to a small reduction in the inventory of solids. In the last period shown in Figure 2, the inventory of solids in the system was increased by re-injecting solids taken from the secondary cyclones. This increased the SO_2 capture efficiency to a value of 1 as no SO_2 was detected at the exit of the carbonator. At the beginning of this period,

CO₂ capture efficiency also increased. The carbonator temperature then rose, as a result of which a decrease in CO₂ capture efficiency was observed.

Figure 2. Results of an experimental run during a SO₂-CO₂ co-capture test (average gas velocity=2.5 m/s, CO₂ inlet fraction=0.12, X_{ave} =0.06).

The experimental results shown in the Results and Discussion section correspond to steady states of at least 10 minutes, such as those shown in Figure 2. These steady periods are characterized by the average reactor temperatures (carbonator and calciner), the inventory of

solids in the risers (carbonator and calciner), the CO₂ and SO₂ concentration at the carbonator inlet, the carbonate content of the solids leaving the carbonator (X_{carb}) and the calciner (X_{calc}), the sulphate content of the solids (X_{CaSO_4}), the average CO₂ carrying capacity of the solids in the system (X_{ave}) and the circulation rate of the solids in the carbonator. A total of 40 hours of useful operation in SO₂ and CO₂ capture mode was achieved.

RESULTS AND DISCUSSION

To analyze SO₂ capture in the carbonator, we followed a similar approach to that used by Alonso et al.³¹, Rodriguez et al.⁵ and Charitos et al.⁶ when analysing CO₂ capture in a CFB carbonator. These previous studies demonstrated that the assumptions of instantaneous and perfect mixing of solids and plug flow in the gas phase are sufficient for interpreting the results obtained in the 30 kWt dual fluidized bed pilot plant. The overall mass balance in the carbonator for SO₂ can be expressed as:

$$\left(\begin{array}{c} \text{SO}_2 \text{ reacting} \\ \text{with CaO in the bed} \end{array} \right) = \left(\begin{array}{c} \text{SO}_2 \text{ removed} \\ \text{from the gas phase} \end{array} \right) = \left(\begin{array}{c} \text{CaSO}_4 \text{ formed in the} \\ \text{circulating stream of CaO} \end{array} \right) \quad (1)$$

According to this mass balance, the SO₂ that is removed from the flue gas fed to the carbonator is equal to the CaSO₄ formed in the circulating stream of CaO. Therefore, in a stationary state:

$$F_{\text{Ca}} \times \Delta X_{\text{CaSO}_4} = E_{\text{sulf CB}} \times F_{\text{SO}_2} \quad (2)$$

where F_{SO_2} is the molar flow of SO_2 fed into the carbonator (mol s^{-1}), $E_{\text{sulf CB}}$ is the SO_2 capture efficiency in the carbonator, F_{Ca} is the Ca molar circulation rate (mol s^{-1}) through the carbonator, and ΔX_{CaSO_4} the increment in molar sulfate content between the inlet and the outlet of the carbonator. The closure of this mass balance is difficult to verify in practice as ΔX_{CaSO_4} is very small, due to the incremental concentration of $CaSO_4$ per cycle considering the high circulation of solids compared to the amount of SO_2 fed into the carbonator²⁰. However, in a continuous system, where there is a make-up flow of fresh limestone and a purge of spent sorbent, a similar mass balance can be applied to the whole Ca-looping system:

$$F_0 \times X_{CaSO_4} = E_{\text{sulf CB}} F_{SO_2} + E_{\text{sulf CC}} F_{SO_2 \text{comb}} \quad (3)$$

where F_0 is the molar flow of make up flow (mol s^{-1}), X_{CaSO_4} is the $CaSO_4$ content in the purge of solids, $F_{SO_2 \text{comb}}$ is the molar flow of SO_2 produced during the combustion of coal in the calciner (mol s^{-1}) and $E_{\text{sulf CC}}$ is the SO_2 capture efficiency in the calciner. In the case of the test carried out in the 30 kWt dual fluidized pilot plant, there is no continuous addition of fresh limestone to the system which would result in an increase in $CaSO_4$ content of the solids circulating in the system. Therefore, the evolution of the X_{CaSO_4} with time during a given experiment with a stable inventory of material in the system can be calculated by using the following expression:

$$X_{CaSO_4} = \int_0^t \frac{F_{SO_2} E_{\text{sulf CB}} + F_{SO_2 \text{comb}} E_{\text{sulf CC}}}{N_{Ca, \text{total}}} dt \quad (4)$$

where $N_{\text{Ca, total}}$ is the amount of Ca present the system (mol). Figure 3 shows a comparison of the experimental sulfate content of samples taken periodically during an experimental run using a batch of limestone with the sulphate content calculated using Eq. 4. As can be seen from this figure, there is a good agreement between the experimental and calculated values, which indicates that there is an adequate mass balance closure between the SO_2 disappearing from the gas phase and the CaSO_4 formed inside the mass of solids present in the system. Figure 3 also indicates a good overall mixing of the solids in the system (with a time scale of minutes to tens of minutes affecting the total inventory of the solids in the system). It should also be noted that CaSO_4 is mainly formed in the carbonator, due to low sulfur content of the coal used and that the X_{CaSO_4} content in the solids taken from calciner and carbonator are similar.

Figure 3. SO_2 mass balance closure. Comparison of the experimental and calculated X_{CaSO_4} in the particles taken from the system during an experimental run.

To analyse the influence of the variables involved in SO₂ capture with a view to the designing of the carbonator, the most interesting mass balance is that of the SO₂ reacting with the bed of solids. This can be written as:

$$E_{\text{sulf CB}} \times F_{\text{SO}_2} = N_{\text{Ca active}} \left(\frac{dX_{\text{CaSO}_4}}{dt} \right)_{\text{reactor}} \quad (5)$$

where $N_{\text{Ca active}}$ is the inventory of Ca (mol) reacting in the carbonator bed and $(dX_{\text{CaSO}_4}/dt)_{\text{reactor}}$ is the average reaction rate of the solids (s⁻¹). Regarding the reaction term, we have shown in a previous work³² that the layer of CaSO₄ is able to grow around the particle surface of cycled CaO without experiencing any geometrical restrictions for low conversion and that the sulfation conversion can be described adequately using a homogeneous model as the random pore model. We also have shown that the surface area available for the sulfation reaction can be correlated adequately with the CO₂ carrying capacity of the sorbent. In order to simplify the reaction term, we have assumed that the solids react in the carbonator bed according to the following expression:

$$\left(\frac{dX_{\text{CaSO}_4}}{dt} \right)_{\text{reactor}} = k_{\text{sulf}} \phi_{\text{SO}_2} X_{\text{ave}} \overline{v_{\text{SO}_2}} \quad (6)$$

where k_{sulf} is the sulfation rate constant, ϕ_{SO_2} is the gas-solid contacting effectivity factor (similar to that defined by Rodríguez et al.⁵ for the CO₂ reaction rate in the carbonator), X_{ave} is the average CO₂ carrying capacity of the solids and $\overline{v_{\text{SO}_2}}$ is the average SO₂ molar fraction in the carbonator. This expression used for the reaction rate term is consistent with the results obtained

in a TGA during the sulfation of cycled CaO under carbonation conditions reported by Arias et al.³² for low sulfation conversions when particles react in a chemically controlled regime.

Regarding the inventory of Ca reacting with SO₂ in the carbonator, it is assumed that the fraction of partially carbonated CaO does not play an active role in SO₂ capture since it is unlikely that SO₂ will react directly with CaCO₃ to produce CaSO₄ at carbonator temperatures of around 650 °C³³. Moreover, the particles that are covered by the layer of CaCO₃ cannot be considered active as the low diffusivity of SO₂ through the carbonate layer at the relatively low temperature of the carbonator would prevent any conversion of the inner CaO inside the particles. On the basis of these assumptions, it is inferred that only those particles that do not reach their maximum CO₂ carrying capacity in the carbonator bed are active for SO₂ retention. This definition of our active inventory is similar to that used by Alonso et al.³¹ and Charitos et al.⁶ for analyzing the CO₂ in a CFB carbonator. Assuming a perfect mixing of the solids in the carbonator, Alonso et al.³¹ defined in a previous work a characteristic time, t*, (which depends on the reactivity of the particles towards CO₂ in the carbonator). According to their definition, this parameter is the time needed for the particles to reach X_{ave} under the reaction conditions in the carbonator and can be calculated using the equation:

$$t^* = \frac{X_{ave} - X_{calc}}{k_{carb} \phi_{CO_2} X_{ave} (v_{CO_2} - v_{CO_2eq})} \quad (7)$$

where k_{carb} is the carbonation rate constant (s⁻¹) and φ_{CO₂} is the gas-solid contacting effectivity factor for the CO₂ (see references^{6,31} for more details). It is assumed that those particles with a residence time in the carbonator higher than t* have achieved their maximum CO₂ carrying capacity and do not react with SO₂. Assuming a perfect mixing of the solids in the carbonator

reactor, a fraction of active solids (f_a), defined as those solids with a residence time in the carbonator lower than t^* , can be calculated using the equation:

$$f_a = 1 - e^{\left(\frac{-t^*}{N_{Ca}/F_{Ca}}\right)} \quad (8)$$

where N_{Ca} is the amount of Ca (mol) in the carbonator and F_{Ca} is the circulation of Ca between the reactors (mol s^{-1}). Using this approach, Charitos et al.⁶ defined an active space time as $\tau_{aCO_2} = N_{Ca} f_a X_{ave}/F_{CO_2}$, from which it follows that the CO_2 capture efficiency parameter is:

$$E_{carb} = k_{carb} \phi_{CO_2} \left(\overline{v_{CO_2}} - v_{CO_2eq} \right) \tau_{aCO_2} \quad (9)$$

From the SO_2 mass balance and the definition of the active inventory of solids as $N_{Ca, active} = N_{Ca} f_a$, Eq. 5 can be re-written in a similar form to that defined for CO_2 to give the following expression:

$$E_{sulf CB} = k_{sulf} \phi_{SO_2} \overline{v_{SO_2}} \tau_{aSO_2} \quad (10)$$

where τ_{aSO_2} is the active space time for the SO_2 and is defined as:

$$\tau_{aSO_2} = \frac{N_{Ca} f_a X_{ave}}{F_{SO_2}} \quad (11)$$

The term $k_{\text{sulf}} \phi_{\text{SO}_2}$ was calculated by comparing both terms of the SO_2 mass balance in Eq. 5. Figure 4 shows a comparison of the SO_2 removed from the gas phase (y-axis) and the SO_2 that reacts with CaO in the carbonator bed of solids (x-axis).

Figure 4. Comparison of the SO_2 removed from the gas phase with the SO_2 that reacts with CaO in the bed of the carbonator.

The apparent sulfation reaction constant, $k_{\text{sulf}} \phi_{\text{SO}_2}$, obtained from the fitting of the results shown in Figure 4 is 3.22 s^{-1} . To determine $k_{\text{sulf}} \phi_{\text{SO}_2}$ only those points with an $E_{\text{Sulf CB}}$ below 1 were used. In order to calculate the value of ϕ_{SO_2} , we employed a value of k_{sulf} from the experimental data presented by Arias et al.³² for Compostilla limestone which has a value of 3.78 s^{-1} at a temperature of $630 \text{ }^\circ\text{C}$ (average temperature for the experimental data obtained in this

work). This yields a ϕ_{SO_2} value of 0.85 which indicates that SO_2 capture in the carbonator in the presence of CO_2 is mainly controlled by the sulfation reaction rate of the particles in the bed.

In Figure 5, SO_2 capture efficiency is plotted against SO_2 active space time. As can be seen, there is reasonable agreement between the experimental results and the values predicted with Eq. 10. From this plot it is deduced that a minimum value of $\tau_{a \text{ SO}_2}$ is needed to achieve certain SO_2 capture efficiency. For example, in order to remove 99 % of the SO_2 fed into the carbonator, an active SO_2 space time of 480 s is needed.

Figure 5. Comparison of experimental SO_2 capture efficiency vs. active space time for SO_2 (solid line calculated from Equation 10 and the following average conditions; carbonator temperature=630 °C; SO_2 inlet concentration=3000 ppmv, gas velocity inlet=2.7 m/s).

It may also be worthwhile to consider the relationships between CO₂ capture efficiency and SO₂ capture efficiency arising from the mass balance equations that lead to Eqs. 9 and 10. As mentioned above, the experimental CO₂ capture efficiency results obtained in this work in the co-capture SO₂ tests were not the main subject of the present work, as the reactor conditions selected for measuring SO₂ capture efficiencies lower than 1 lead to very modest CO₂ capture efficiencies. Nevertheless, the data on CO₂ capture efficiencies obtained during these tests were analyzed using the methodology proposed by Charitos et al.⁶ and Eq. 9 in order to obtain an apparent carbonation reaction constant, $k_{\text{carb}} \phi_{\text{CO}_2}$. This constant was 0.33 s⁻¹, which is consistent with the value reported by Charitos et al.⁶ of 0.43 s⁻¹ using experimental data acquired in the 30-kW INCAR-CSIC pilot plant using a different batch of the same limestone. Combining Eqs. 9 and 10, we obtain:

$$E_{\text{sulf CB}} = \frac{k_{\text{sulf}} \phi_{\text{SO}_2} \overline{v_{\text{SO}_2}} F_{\text{CO}_2}}{k_{\text{carb}} \phi_{\text{CO}_2} (v_{\text{CO}_2} - v_{\text{CO}_2\text{eq}}) F_{\text{SO}_2}} E_{\text{carb}} \quad (12)$$

Figure 6 compares the experimentally measured CO₂ and SO₂ capture efficiencies achieved in the 30 kW_{th} pilot plant with this equation, using the constants reported above. As can be seen there is reasonable agreement between the experimental and calculated values. When the carbonator is operating in experimental conditions that allow a typical CO₂ capture efficiency of above 0.8, virtually all the SO₂ fed into this reactor is removed from the flue gas. Only when the operating conditions in the carbonator yield a CO₂ capture efficiency that is well below 0.5, will the SO₂ capture efficiency be lower than 1. Since the main target in the carbonator is to remove CO₂ at high capture efficiencies (even if this is at the expense of large make-up flow of sorbent to ensure the presence of a sufficient inventory of active material in the bed), it can be assumed

that almost total desulfurization of the flue gas will take place in the carbonator of a Calcium Looping CO₂ capture system.

Figure 6. Comparison between the experimental results of SO₂ capture efficiency and CO₂ capture efficiency (line corresponds to the values calculated using Eq. 12).

CONCLUSIONS

The retention of SO₂ during CO₂ capture in a CFB carbonator of dual fluidized bed experimental facility working in continuous mode has been studied. The results obtained show that CFB carbonators are excellent desulfurization units and SO₂ capture efficiencies of above 0.95 can be achieved, even with low inventories of solids in the reacting bed. A good closure of the SO₂ mass balance of the SO₂ during its removal from the gas phase and its reaction with the

inventory of solids was found. A simple reactor model was applied to predict SO₂ capture efficiency. The apparent sulfation reaction constant for the limestone used in this work was 3.22 s⁻¹. From this value, it was calculated that a gas-solid contact factor of around 0.85 was calculated, indicating that SO₂ capture efficiency is controlled by the chemical sulfation reaction. The results obtained in this work show that when the carbonator is working with a typical CO₂ capture efficiency of above 0.8, the SO₂ entering with the flue gas will be removed from the flue gas that if fed in.

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NOTATION

E_{carb}	CO ₂ capture efficiency
$E_{\text{sulf CB}}$	SO ₂ capture efficiency in the carbonator
$E_{\text{sulf CC}}$	SO ₂ capture efficiency in the calciner
F_0	molar make up flow of limestone (mol/s)
f_a	fraction of active particles reacting in the carbonator
F_{Ca}	molar flow of Ca circulating between reactors (mol/s)
F_{CO_2}	molar flow of CO ₂ fed to the carbonator (mol/s)
F_{SO_2}	molar flow of SO ₂ fed to the carbonator (mol/s)
$F_{\text{SO}_2 \text{ comb}}$	molar flow of SO ₂ produced during coal combustion (mol/s)
k_{carb}	carbonation rate constant (s ⁻¹)
k_{sulf}	sulfation rate constant (s ⁻¹)
N_{Ca}	inventory of Ca in the carbonator bed (mol)
$N_{\text{Ca, active}}$	inventory of active Ca in the carbonator bed (mol)
$N_{\text{Ca, total}}$	total inventory of Ca in the system (mol)
t^*	characteristic time (s)
X_{ave}	maximum CO ₂ carrying capacity of the solids
X_{calc}	carbonate content of the solids leaving the calciner
X_{carb}	carbonate content of the solids leaving the carbonator
X_{CaSO_4}	sulfate content of the solids
<i>Greek symbols</i>	
ΔX_{CaSO_4}	increment of molar sulfate content of the solids in the carbonator
ϕ	gas-solid contacting effectivity factor
v	molar fraction
τ_a	active space time (s)

REFERENCES

- (1) Abanades, J.C.; Anthony, E.J.; Lu, D.Y.; Salvador, C.; Álvarez, D. Capture of CO₂ from Combustion Gases in a Fluidized Bed of CaO. *AIChE Journal* **2004**, *50*, 1614.
- (2) Lu, D.Y.; Hughes, R.W.; Anthony, E.J. Ca-based sorbent looping combustion for CO₂ capture in pilot-scale dual fluidized beds. *Fuel Processing Technology* **2008**, *89*, 1386.
- (3) Alonso, M., Rodríguez, N., González, B.; Grasa, G.; Murillo, R.; Abanades J.C. Carbon dioxide capture from combustion flue gases with a calcium oxide Chemicals loop. Experimental results and process development. *Int. Journal of Greenhouse Gas Control* **2010**, *4*, 167.

- (4) Charitos, A.; Hawthorne, C.; Bidwe, A.R.; Sivalingam, S.; Schuster, A.; Spliethoff, H.; Scheffknecht, G. Parametric investigation of the calcium looping process for CO₂ capture in a 10 kW_{th} dual fluidized bed. *International Journal of Greenhouse Gas Control* **2010**, *4*, 776.
- (5) Rodríguez, N.; Alonso, M.; Abanades, J.C. Experimental investigation of a circulating fluidized-bed reactor to capture CO₂ with CaO. *AIChE Journal* **2011**, *57*, 1356.
- (6) Charitos, A.; Rodríguez, N.; Hawthorne, C.; Alonso, M.; Zieba, M.; Arias, B.; Kopanakis, G.; Scheffknecht, G.; Abanades, J.C. Experimental validation of the calcium looping CO₂ capture process with two circulating fluidized bed carbonator reactors. *Ind. Eng. Chem. Res.* **2011**, *50*, 9685.
- (7) Hawthorne, C.; Dieter, H.; Bidwe, A.; Schuster, A.; Scheffknecht, G.; Unterberger, S.; Käß, M.; CO₂ Capture with CaO in a 200 kW_{th} Dual Fluidized Bed Pilot Plant, *Energy Procedia* **2011**, *4*, 441.
- (8) Sánchez-Biezma, A.; Ballesteros, J.C.; Díaz, L.; de Zárraga, E.; Álvarez, F.J.; López, J.; Arias, B.; Grasa, G.; Abanades, J.C. Postcombustion CO₂ capture with CaO. Status of the technology and next steps towards large scale demonstration. *Energy Procedia* **2011**, *4*, 852.
- (9) Sánchez-Biezma, A.; Díaz, L.; López, J.; Arias, B.; Paniagua, J.; De Zárraga, E.; Álvarez, F.J.; Abanades, J.C. La Pereda CO₂: a 1.7 MW pilot to test post-combustion CO₂ capture with CaO. *21st International Conference on Fluidized Bed Combustion*, Naples (Italy), June 3-6, **2012**.
- (10) Plötz, S.; Bayrak, A.; Galloy, A.; Kremer, J.; Orth, M.; Wieczorek, M.; Ströhle, J.; Epple, B. First Carbonate Looping Experiments with a 1 MW_{th} Test Facility Consisting of Two Interconnected CFBs. *21st Conference on Fluidized Bed combustion*, Naples, Italy, June 3-6, **2012**.
- (11) Shimizu, T.; Hirama, T.; Hosoda, H.; Kitani, K.; Inagaki, M.; Tejima, K. A twin fluid-bed reactor for removal of CO₂ from combustion processes. *Trans. IChemE* **1999**, *77*, 63.
- (12) Romeo, L.M.; Abanades, J.C.; Escosa, J.M.; Paño, J.; Jiménez, A.; Sánchez-Biezma, A.; Ballesteros, J.C. Oxyfuel carbonation/calcination cycle for low cost CO₂ capture in existing power plants. *Energy Conversion Management* **2008**, *49*, 2809.
- (13) Romano, M. Coal-fired power plant with calcium oxide carbonation for post-combustion CO₂ capture. *Energy Procedia* **2009**, *1*, 1099.

- (14) Ströhle, J.; Lasheras, A.; Galloy, A.; Epple, B. Simulation of the carbonate looping process for post-combustion CO₂ capture from a coal-fired power plant. *Chem. Eng. Technol.* **2009**, *32*, 435.
- (15) Yongping, Y.; Rongrong, Z.; Liqiang, D.; Kavosh, M.; Patchigolla, K.; Oakey, J. Integration and evaluation of a power plant with a CaO-based CO₂ capture system. *Int. Journal of Greenhouse Gas Control* **2010**, *4*, 603.
- (16) Martínez, I.; Murillo, R.; Grasa, G.; Abanades, J.C. Integration of Ca looping system for CO₂ capture in existing power plants. *AIChE Journal* **2010**, *57*, 2599.
- (17) Anthony, E.J.; Granatstein, D.L. Sulfation phenomena in fluidized bed combustion systems. *Progress in Energy and Combustion Science* **2001**, *27*, 215.
- (18) Li, Y.; Buchi, S.; Grace, J.R.; Lim, C.J. SO₂ removal and CO₂ capture by limestone resulting from calcination/sulfation/carbonation cycles. *Energy & Fuels* **2005**, *19*, 1927.
- (19) Ryu, H-J.; Grace, J.R.; Lim, C.J. Simultaneous CO₂/SO₂ capture characteristics of three limestones in a fluidized-bed reactor. *Energy & Fuels* **2006**, *20*, 1621.
- (20) Grasa, G.S.; Alonso, M.; Abanades J.C. Sulfation in a carbonation/calcination loop to capture CO₂. *Ind. Eng. Chem. Res.* **2008**, *47*, 1630.
- (21) Sun, P.; Grace, J.R.; Lim, C.J.; Anthony, E.J. Removal of CO₂ by calcium-based sorbents in presence of SO₂. *Energy & Fuel* **2007**, *21*, 163.
- (22) Manovic, V.; Anthony, E.J. Sequential SO₂/CO₂ capture enhanced by steam reactivation of CaO-based sorbent. *Fuel* **2008**, *87*, 1564.
- (23) Manovic, V.; Anthony, E.J.; Loncarevic, D. SO₂ retention by CaO-based sorbent spent in CO₂ looping cycles. *Ind. Eng. Chem. Res.* **2009**, *48*, 6617.
- (24) Pacciani, R.; Müller, C.R.; Davidson, J.F.; Dennis, J.S.; Hayhurst, A.N. Performance of novel synthetic Ca-based sorbent suitable for desulfurizing flue gases in a fluidized bed. *Ind. Eng. Chem. Res.* **2009**, *48*, 7016.
- (25) Manovic, M.; Anthony, E.J. Competition of sulphation and carbonation reactions during looping cycles for CO₂ capture by CaO-based sorbents. *J. Phys. Chem. A* **2010**, *114*, 3397.
- (26) Abanades, J.C.; Rubin, E.S.; Anthony, E.J. Sorbent cost and performance in CO₂ capture systems. *Ind. Eng. Chem. Res.* **2004**, *43*, 3462.

- (27) Dean, C.C.; Blamey, J.; Florin, N.H.; Al-Jeboori, M.J.; Fennell, P.S. The calcium looping cycle for CO₂ capture from power generation, cement manufacture and hydrogen production. *Chemical Engineering Research and Design* **2011**, 89, 836.
- (28) Dean, C.C.; Dugwell, D.; Fennell, P.S. Investigation into potential synergy between power generation, cement manufacture and CO₂ abatement using the calcium looping cycle. *Energy & Environmental Science* **2011**, 4, 2050.
- (29) Jia, L.; Hughes, R.; Lu, D.; Anthony, E.J.; Lau, I. Attrition of calcining limestones in circulating fluidized-bed systems. *Ind. Eng. Chem. Res.* **2007**, 46, 5199.
- (30) Coppola, A.; Montagnaro, F.; Salatino, P.; Scala, F. Fluidized bed calcium looping: The effect of SO₂ on sorbent attrition and CO₂ capture capacity. *Chemical Engineering Journal* **2012**, 207-208, 445.
- (31) Alonso, M.; Rodríguez, N.; Grasa, G.; Abanades, J.C. Modelling of a fluidized bed carbonator reactor to capture CO₂. *Chemical Engineering Science* **2009**, 64, 883.
- (32) Arias, B.; Cordero, J.M.; Alonso, M.; Abanades, J.C. Sulfation Rates of Cycled CaO Particles in the Carbonator of a Ca-Looping Cycle for Postcombustion CO₂ Capture. *AIChE Journal* **2012**, 58, 2262.
- (33) Hu, G.; Dam-Johansen, K.; Wedel, S.; Hansen, J.P. Review of the direct sulfation reaction of limestone. *Progress in Energy and Combustion Science* **2006**, 32, 386.