The effect of SO_2 and H_2O during Calcium Looping for CO_2 Capture in a Twin Fluidized Bed Reactor System

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Highlights

- SO_2 negatively affected the sorbent CO_2 capture capacity.
- A positive role of steam was observed in enhancing the sorbent CO_2 capture capacity.
- A complex effect of the carbonator atmosphere on sorbent attrition was found.

1. Introduction

The Calcium Looping (CaL) process carried out in dual interconnected Fluidized Bed (FB) systems is a technique able to treat CO_2-containing combustion flue gases following the concept of "carbon capture & storage". It is based on the alternated temperature-swing CO_2 uptake, with CO_2 capture taking place in a carbonator operated at around 650–700°C followed by the release of concentrated CO_2 in a calciner operated at around 900–950°C, according to the reversible reaction $CaO_{(s)}+CO_{2(g)}=CaCO_{3(s)}$ [1]. CaL efficiency is affected by sorbent thermal sintering (deactivation) upon iterated looping and by particle attrition and fragmentation. The relevance of these phenomena has been addressed in the recent literature [2]. A somewhat less investigated aspect is represented by the possible concurrent effect of steam and sulfur dioxide. These two species are usually both present in the combustion flue gas to be decarbonized, in amounts depending on the fuel properties and on the upstream process conditions. It has been suggested that steam can enhance, upon carbonation, CO_2 diffusion through the sorbent particle to reach reactive CaO [3–7]. On the other hand, the presence of SO_2 would deplete CaO otherwise available for CO_2 capture, following the sulfation reaction of CaO to give $CaSO_4$ [1,8]. In addition, the sulfation reaction is non-reversible under the operating conditions of the calciner. This means that: i) CaO reacted with SO_2 is definitively lost for CO_2 capture; ii) the (low-porous) $CaSO_4$-based particle shell adds to the $CaCO_3$-based one in hindering the contact between CO_2 and CaO upon carbonation. This work aims at giving a further contribution on this topic. To this end, a lab-scale twin FB system [9] – set up to mimic the thermal history of sorbent particles typical of large-scale CaL operating conditions – was operated with a reference limestone under different fluidizing atmospheres. The effect of the presence of steam and of sulfur dioxide, considered either alone or together, is discussed in terms of CO_2 capture capacity of the sorbent, its tendency to undergo attrition, and its microstructural properties.

2. Methods

The used sorbent was a German limestone, EnBW, nearly pure in $CaCO_3$ and very reactive [2]. An initial batch of 20 g of sorbent (sieved in the 0.4–0.6 mm particle size range) was fed to the system and diluted in coarser (0.9–1 mm) inert silica sand. Each CaL test consisted in ten calcination/carbonation cycles, plus a final calcination stage. The calciner was operated at 940°C with a fluidizing atmosphere containing 70% CO_2 (in air). Each calcination stage lasted 20 min. The carbonator was operated at 650°C, and each stage lasted 15 min. Six different operating conditions were investigated by changing the fluidizing atmosphere upon carbonation. A concentration of 15% CO_2 was kept in each case, the rest being: i-*dry*) air, no steam & SO_2; ii-*dry sulfur-poor DSP*) air/N_2 plus 75 ppm SO_2, to mimic a case in which quite efficient desulfurisation of flue gas generated from the combustion of a regular coal occurred upstream CaL, no steam; iii-*dry sulfur-rich DSR*) air/N_2 plus 1500 ppm SO_2, to mimic a case in which no desulfurisation of flue gas occurred upstream CaL, no steam; iv-*stecar*) air plus 10% steam, no SO_2; v-*stecar sulfur-poor SCSP*) air/N_2 plus 10% steam and 75 ppm SO_2; vi-*stecar sulfur-rich SCSR*) air/N_2 plus 10% steam and 1500 ppm SO_2. Analysis of the flue gas composition at the carbonator exit allowed to calculate the CO_2 capture capacity of the sorbent expressed as ξ, the mass of CO_2 captured per initial mass of sorbent. Additional characterizations consisted in the evaluation of the sorbent attrition tendency by capture of elutriated fines, particle size distribution analysis of in-bed sorbent fragments, scanning electron microscopy and N_2 porosimetry analyses.

3. Results and discussion

Figure 1 shows the sorbent performance results in terms of ξ as a function of the number of carbonation stages for the six operating conditions under investigation. In the base case (*dry*) ξ decreased from 0.193 to 0.049 g/g due to the effect of thermal sintering as the number of cycles increased (this effect was observed for any condition). When SO_2 was added upon carbonation (cases *DSR* and *DSP*), the sorbent capacity decreased and the detrimental effect was larger when the SO_2 concentration was higher: ξ decreased from 0.170 to 0.032 g/g (*DSP*), from 0.143 to 0.008 g/g (*DSR*). When steam was added (*stecar* vs. *dry*) the sorbent capacity increased: ξ was 0.199 g/g after the 1st carbonation, 0.054 g/g after the 10th. The presence of SO_2, when limited (*SCSP* vs. *stecar*), did not significantly affect ξ after the first cycles (the positive effect of the presence of steam somewhat counterbalanced the negative one related to SO_2) but ξ was negatively influenced by SO_2 in the later stages of the process. On the other hand, the presence of SO_2 in higher amount (*SCSR* vs. *stecar*) determined a relevant loss of performance: ξ decreased from 0.191 g/g to 0.020 g/g.

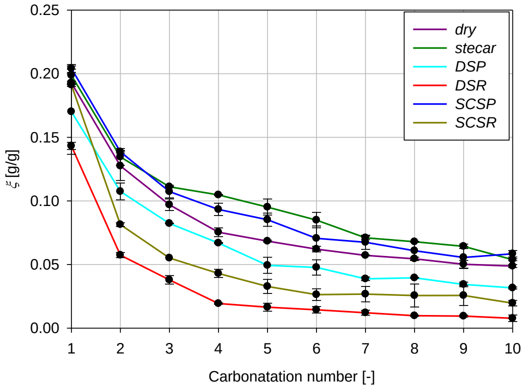

Figure 1. CO_2 capture capacity of the sorbent along carbonation stages for the six carbonation conditions.

4. Conclusions

The positive role of steam in enhancing the CO_2 capture capacity of sorbent even in presence of SO_2 was observed. High concentrations of SO_2 in the carbonator should be avoided by means of proper desulfurisation of the combustion flue gas. Further results showed the complex effect that the carbonator atmosphere – through the promotion of the formation of mechanically hard species ($CaCO_3$/$CaSO_4$), and the weakening effect related to the presence of steam – had on the sorbent attrition tendency.

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Keywords
Calcium Looping; Limestone; Fluidized bed; Attrition.