The effect of SO$_2$ and H$_2$O 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-stearc) air plus 10% steam, no SO$_2$; v-stearc sulfur-poor SCSP) air/N$_2$ plus 10% steam and 75 ppm SO$_2$; vi-stearc 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 CO₂ capture capacity of the sorbent expressed as $\xi$, the mass of CO₂ 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 N₂ porosimetry analyses.

3. Results and discussion

Figure 1 shows the sorbent performance results in terms of $\xi$ as a function of the number of carbonation stages for the six operating conditions under investigation. In the base case (dry) $\xi$ 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 SO₂ was added upon carbonation (cases DSR and DSP), the sorbent capacity decreased and the detrimental effect was larger when the SO₂ concentration was higher: $\xi$ 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: $\xi$ was 0.199 g/g after the 1st carbonation, 0.054 g/g after the 10th. The presence of SO₂, when limited (SCSP vs. stecar), did not significantly affect $\xi$ after the first cycles (the positive effect of the presence of steam somewhat counterbalanced the negative one related to SO₂) but $\xi$ was negatively influenced by SO₂ in the later stages of the process. On the other hand, the presence of SO₂ in higher amount (SCSR vs. stecar) determined a relevant loss of performance: $\xi$ decreased from 0.191 g/g to 0.020 g/g.

![Graph showing CO₂ capture capacity vs. carbonation stages for six conditions](image)

Figure 1. CO₂ capture capacity of the sorbent along carbonation stages for the six carbonation conditions.

4. Conclusions

The positive role of steam in enhancing the CO₂ capture capacity of sorbent even in presence of SO₂ was observed. High concentrations of SO₂ in the carbonator should be avoided by means of proper desulphurisation 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 (CaCO₃/ CaSO₄), and the weakening effect related to the presence of steam – had on the sorbent attrition tendency.

References


Keywords
Calcium Looping; Limestone; Fluidized bed; Attrition.