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How Does the Concentration of CO_2 Affect Its Uptake by a Synthetic Ca-Based Solid Sorbent?

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Introduction

Growing concern about greenhouse gases such as CO_2 in the atmosphere has encouraged the development of processes for generating electricity from fossil fuels, such as coal, with zero, or near-zero, emissions of CO_2 and other pollutants. In particular, owing to the ongoing need to produce a significant proportion of electricity from coal, new ways of utilizing coal are being sought. One possibility[1] is to hydrogasify coal in H_2 at a high pressure and temperature (~7 MPa, ~850°C) to produce CH_4 in: $C_{(s)} + 2H_2 \rightarrow CH_4$. The resulting CH_4 can be catalytically reformed by steam in $CH_4 + H_2O \rightarrow CO + 3H_2$, with the water-gas equilibrium $CO + H_2O = CO_2 + H_2$ operating. One feature of such a process is that if it occurs in the presence of a solid sorbent containing CaO, the CO_2 can be removed in: $CaO + CO_2 \rightarrow CaCO_3$ ($\Delta H^0_{1023} = -169$ kJ/mol). This moves the water-gas equilibrium almost completely to the right, thereby producing H_2 uncontaminated by CO_2. The net result is 4 moles H_2, two of which can be exported and two returned to maintain hydrogasification.[1] Of course other routes to give syngas exist, e.g. direct steam gasification of coal. By subsequently heating the $CaCO_3$, the bound CO_2 is released as an almost pure stream of CO_2 for disposal, e.g. underground or in deep saline aquifers. The reaction of CaO with CO_2 has also been envisaged for other applications, e.g., for extracting CO_2 directly from the atmosphere.[2] The cost of separating and compressing CO_2 from the flue gases of power plants amounts to 50–80% of the overall cost[3] of capturing and storing CO_2. Therefore, a solid sorbent for CO_2 must be able to remain highly reactive for a large number of cycles of carbonation and calcination, for its use to be economically viable.

The use of Ca-based sorbents, both natural, such as limestone and dolomite,[4,5] and synthetic,[6–8] for removing CO_2 has been studied extensively. Limestone and dolomite are known[5,9,10] to deactivate after increasing number of cycles of carbonation and calcination, mainly because of sintering at the temperatures of interest. In fact, their uptake of CO_2 has been found[4,5] to be limited by the volume available inside pores narrower than 200 nm. Several authors[4,11–13] have tried to increase the CO_2 uptake of calcined limestone by carbonating it in high partial pressures of CO_2; however, its uptake has generally proved[4,11–13] to be independent of the partial pressure of CO_2.

By contrast, the effect of the concentration of CO_2 on the uptake by a synthetic sorbent, when subjected to cycles of calcination and carbonation has received limited attention. Here, a preliminary study is presented on the effect of the concentration of CO_2 on the uptake of a synthetic Ca-based sorbent, prepared by hydrolyzing CaO. Its performance is compared below with that of a natural sorbent, dolomite, subjected to the same regimes of reaction.

Experimental

Materials

The synthetic sorbent HA-85-850, consisting of 85 wt % CaO and 15 wt % $Ca_{12}Al_{14}O_{33}$ (mayenite), was prepared following the protocol of Li et al.[7] Mayenite is a mixed oxide, resulting from the solid-state reaction of CaO and Al_2O_3 between 800 and 1000°C. Reagent grade powdered CaO (Fisher U.K.) was added to an aqueous solution of $Al(NO_3)_3$ in a mixture of 75 vol % water and 25 vol % 2-propanol. The amounts of CaO and the nitrate were chosen such that the mass ratio of CaO to mayenite was 85:15, an optimum suggested by previous work.[8] The solution, maintained at 75°C, was stirred using a magnetic stirrer at 700 rpm for 1 h and then evaporated to dryness in an oven at 120°C. The resulting cake was crushed into a fine powder and roasted at 500°C in an oven to decompose the chosen nitrate to its oxide. This three-step procedure was designed so that the water,

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2-propanol, and the nitrates evaporated at different stages, so as to obtain a porous powder. The powder was then made into pellets by adding a little water and stirring the wetted powder to form granules; these were then calcined at 850°C in an oven for 1.5 h.

Naturally occurring dolomite (91% purity, obtained from Steetley, Worksop, UK) was used in the comparative experiments.

Cycling experiments

The two sorbents were ground, sieved to 500–700 μm, and tested in a bench-scale fluidized bed. This consisted of sand ($\sim$20 cm^3 after tapping, d_p = 355–425 μm), contained in a vertical quartz tube (i.d. 29.5 mm and length 460 mm) heated in an electric furnace. The temperature of the bed was measured by a K-type thermocouple (1.5 mm o.d.), suspended above the distributor, a porous frit. The concentration of CO_2 in the gas leaving the bed was measured continuously by a NDIR analyzer (ABB EL3020, range 1–100 mol % CO_2). The precision of the CO_2 analysis, as measured by NDIR, was within 2%. For this $\sim$1 dm^3/min (at room conditions) was sampled via a quartz probe, positioned with its tip 160 mm above the distributor, i.e. about 130 mm above the bed surface. The bed was initially heated to 750°C, while fluidized with N_2 (61.4 cm^3/s at room conditions, giving a vigorously bubbling fluidized bed). When the set temperature was reached, 1.0 g of sorbent particles was placed into a crucible and quickly tipped from the open top of the reactor into the hot bed. The mass was chosen so as to not upset the temperature by more than 5°C, as explained in detail elsewhere.[8] After any CO_2 had been driven off, 10.0 cm^3/s of CO_2 (at room conditions) were then added to the N_2, so that the mole fraction of CO_2 in the fluidizing gas during carbonation, y_{co_2}, was $\sim$0.14. The superficial velocity of the gas, U, was in the range 5.6 to 7.1 times U_{mf}, where U_{mf} is U at incipient fluidization. After 500 s, the CO_2 was switched off again and the sample left to calcine for 500 s in nitrogen. Such a cycle of carbonation and calcination was repeated 43 times. On the 44th cycle, the CO_2 flow rate was increased to 22.7 cm^3/s so that y_{co_2} $\sim$0.27, and kept constant for a further 44 cycles, after which y_{co_2} was finally decreased back to 0.14 and the particles cycled for a further 20 times. These mole fractions exceed the equilibrium mole fraction for CO_2 over CaO at 750°C and 101.3 kPa of $\sim$0.10, so that CO_2 was absorbed by the sorbent. For such a system, it proved easier to achieve the appropriate condition for either carbonation or calcination by changing the concentration of CO_2 while keeping the temperature constant, rather than cycling between two different temperatures.

In a subsequent experiment, a set of nine cycles was performed with a carbonation time, t_{carb}, of 500 s and a calcination time of 500 s; then, t_{carb} was increased to 15 min, and the batch of particles was cycled further for nine times. Then, t_{carb} was increased to 30 min; after a further six cycles, t_{carb} was finally set to 12 h. The temperature was kept constant at 750°C, and y_{co_2} $\sim$0.14 was used. The temperature of the bed, 750°C, the composition of the gas during calcination, 100 mol % N_2, and the calcination time, 500 s, were maintained constant throughout both experiments. Such temperature was chosen so that the rate of both reactions could proceed reasonably rapidly.

Results

Figure 1 is a plot of the mole fraction of CO_2 in the off-gases from a fluidized bed during two complete cycles of carbonation and calcination for a sorbent. The shaded area in Figure 1, when multiplied by the total molar flow rate of the fluidizing gas, gives the number of moles of CO_2, N_{co_2}, released during calcination. This is equal to the number of moles absorbed during the previous carbonation, because calcination was always found to be complete, in that no $CaCO_3$ was found by X-ray analysis in the sorbent after calcination. A detailed discussion of mass balances for this method of experimentation is given elsewhere,[4,8] but typically errors in uptake are within 10%. The value of N_{co_2} can be converted into the uptake, $\overline{X}$, of CO_2 by the sorbent ($\overline{X}$ mass of CO_2/mass of sorbent), assuming no loss of fines by attrition, using $\overline{X} = 44(N_{co_2}/m_o) = m_{co_2}/m_o$, where $m_{CO_2} = 44N_{CO_2}$ is the mass of CO_2 released during calcination, and m_o is the initial mass of the calcined sorbent. The uptake of CO_2 by a sorbent on a mass basis is related to the conversion, X, of its CaO content to $CaCO_3$ by $\overline{X} = Xx_{CaO}(44/56)$, where x_{CaO} is the initial mass fraction of CaO present in a sorbent. The value of x_{CaO} for dolomite, 0.58, is known from the analysis of its composition, whereas the one for HA-85-850, 0.85, is known from the amount of CaO used to make the sorbent; both values were further confirmed using the Rietveld analysis on an XRD measurement of the sorbents.[8]

Figure 2 shows the uptakes of CO_2 for both sorbents during an experiment in which the mole fraction of CO_2 was suddenly altered and subsequently kept steady. The maximum theoretical uptakes for dolomite and HA-85-850 can be calculated using $\overline{X} = X_{CaO}(44/56)$; they are $\overline{X} =$

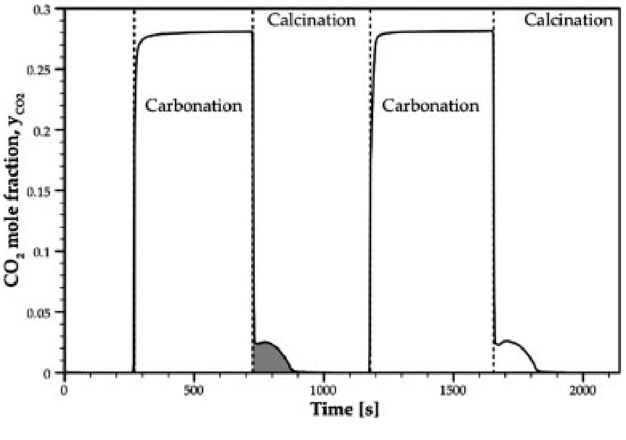

Figure 1. A typical plot showing the mole fraction of CO_2 in the off-gas during two cycles for 1.0 g of HA-85-850.

T = 750°C, m_o =1.00 g, d_p = 500–710 μm, Q_{N_2} = 61.4 cm^3/s, Q_{CO_2} = 22.7 cm^3/s, y_{CO_2} = 0.27, sand d_p = +355–425 μm, U/U_{mf} = 5.6 (without CO_2), 7.1 (with CO_2). Flow rates in cm^3/s are for an environment at 101.3 kPa and 25°C. The shaded area is discussed in the text.

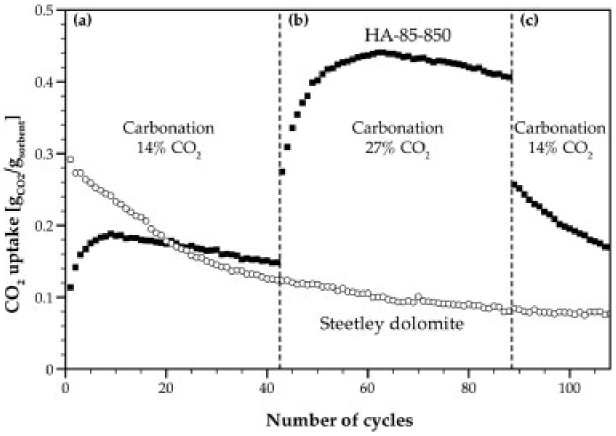

Figure 2. Uptakes for HA-85-850 (■) and Steetley dolomite (○) cycled in the fluidized bed.

T = 750°C, m_o = 1.00 g, d_p = 500–710 μm, Q_{N_2} = 61.4 cm^3/s, Q_{CO_2} = 10.0 or 22.7 cm^3/s, y_{CO_2}= 0.14 or 0.27, sand d_p = +355–425 μm, U/U_{mf} = 5.6 (without CO$_2$), 6.4 or 7.1 (with CO$_2$). Flow rates in cm^3/s are for an environment at 101.3 kPa and 25°C.

0.457 and 0.668 $g_{CO_2}/g_{sorbent}$, respectively. During the first 43 cycles (stage a in Figure 2), with y_{CO_2} = 0.14, the dolomite progressively deactivated after increasing number of cycles, whereas HA-85-850 showed an increase in uptake during the first 5 cycles and then slowly fell in subsequent cycles. Upon increasing y_{CO_2} to 0.27 in the 44th cycle, (stage b in Figure 2), the dolomite did not experience any appreciable change in its uptake of CO$_2$; in fact, it kept decreasing, reaching 0.09 $g_{CO_1}/g_{sorbent}$ at the end of stage b, i.e. after 87 cycles. By contrast, the uptake of HA-85-850, increased markedly after each cycle of the new stage, up to a maximum and then fell to 0.4 $g_{CO_2}/g_{sorbent}$ at the end of stage b. After y_{CO_2} had been decreased back to 0.14 in the 88th cycle, (stage c in Figure 2), the dolomite's uptake, which by then had almost reached a plateau of 0.08 $g_{CO_2}/g_{sorbent}$, was again insensitive to a change in the concentration of CO$_2$. However, the uptake of HA-85-850 fell to 0.25 $g_{CO_2}/g_{sorbent}$ after the 88th cycle, and kept decreasing until it reached 0.17 $g_{CO_2}/g_{sorbent}$ at the end of stage c. Remarkably, in the first cycle of stage c the uptake of HA-85-850 did not drop back to the uptake attained in the last cycle of stage a, i.e. 0.16 $g_{CO_2}/g_{sorbent}$, but achieved the higher value of $g_{CO_2}/g_{sorbent}$, revealing that a portion of the sorbent's capacity for CO$_2$ had been regenerated during stage b.

Previous research has shown that the ultimate uptake of CO$_2$ by a limestone is affected by extending the carbonation time. For example, Lysikov et al.[13] observed that the CO$_2$ uptake of sintered limestone gradually increased from 0.1 to 0.4 $g_{CO_2}/g_{sorbent}$, when the carbonation time was increased from 7.5 to 30 min. Accordingly, the effect of the carbonation time on the uptake and durability of both HA-85-850 and dolomite was investigated here. For this, an experiment was performed in the fluidized bed, in which a batch of sorbent was subjected to cycles of carbonation and calcination for different carbonation times, following the aforementioned procedure with y_{CO_2} = 0.14 at all times. The results are shown in Figure 3. During the first 9 cycles (t_{carb} = 500 s), the uptake of CO$_2$ of HA-85-850 had increased up to 0.3 $g_{CO_2}/g_{sorbent}$. On increasing t_{carb} to 15 min, the uptake of CO$_2$ started increasing again; after a further nine cycles, its uptake reached 0.34 $g_{CO_2}/g_{sorbent}$. After extending the carbonation time to 30 min in the subsequent six cycles, the uptake of CO$_2$ kept increasing, reaching 0.35 $g_{CO_2}/g_{sorbent}$; finally, after 12 h of carbonation, the sorbent attained the highest uptake, i.e. ~0.41 $g_{CO_2}/g_{sorbent}$. In the case of dolomite, carbonating the particles for a longer time also helped to increase its CO$_2$ uptake in subsequent cycles, but to a much lesser extent. This could not prevent, however, the uptake from falling later.

Discussion

The uptake of CO$_2$ by HA-85-850 proved to depend on the concentration of CO$_2$ used in carbonation, as shown in Figure 2 for cycle times likely to be relevant in the industrial application of this technique. This is in striking contrast to the behavior of both dolomite, as reported here, and limestone,[4] cycled under the same regimes of reaction.

Another important feature of HA-85-850 is its fairly constant uptake of CO$_2$ during stage a (see Figure 2), as reported previously.[8] Here, the pore volume of calcined HA-85-850 was measured after various number of cycles, revealing that the stability of CO$_2$ uptake was mainly owing to the retention of pore volume in pores <200 nm after many cycles, i.e. the sorbent did not sinter. Moreover, it should be noted in Figure 2 that, although the uptake of HA-85-850 was markedly smaller than that of dolomite in the early cycles, the synthetic sorbent outperformed the dolomite after only 20 cycles, when y_{CO_2} ~0.14, confirming previous findings.[8]

Figure 2 also shows that the uptake of HA-85-850 increased upon raising the CO$_2$ concentration to 0.27 from 0.14 at the beginning of stage b, i.e. even though the sorbent had already been cycled 43 times. Therefore, not only was the sorbent able to maintain a fairly constant uptake in the first stage of the experiment (stage a), in agreement with previous work,[8] but it was also able to raise its uptake when y_{CO_2} was increased, and maintain the high uptake throughout

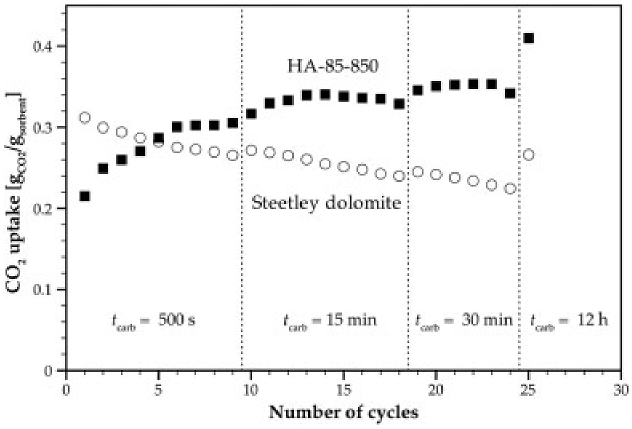

Figure 3. Uptakes for HA-85-850 (■) and Steetley dolomite (○) cycled with different carbonation times in the fluidized bed.

T = 750°C, m_o =1.00 g, d_p = 500–710 μm, Q_{N_2} = 61.4 cm^3/s, Q_{CO_2} = 10.0 cm^3/s, y_{CO_2} = 0.14, sand d_p = +355–425 μm, U/U_{mf} = 5.6 (without CO$_2$), 6.4 (with CO$_2$). Flow rates in cm^3/s are for an environment at 101.3 kPa and 25°C.

stage b. It must also be noted that, when the CO_2 concentration was reduced to 0.14 in stage c, the uptake of HA-85-850 decreased, but to a higher level than that obtained at the same CO_2 concentration in stage a. Thus, it may be that HA-85-850 is able to develop new pore volume when carbonated in higher y_{CO_2}, and therefore enable more CaO to be converted to $CaCO_3$. Further research is being undertaken to explain how the uptake of HA-85-850 depends on y_{CO_2}.

Finally, Figure 3 clearly shows that both sorbents, when cycled in the fluidized bed, attained a higher uptake upon progressively increasing the carbonation time, similar to observations with limestone,[13] although for dolomite the increment in uptake is small. This result is somewhat less surprising; in fact, by extending the carbonation time, more CO_2 can diffuse through the layer of newly formed $CaCO_3$ and reach the uncarbonated CaO in the sorbent, thereby increasing the overall uptake of the sorbent.[9] However, in the case of dolomite, increasing the carbonation time did not prevent it from losing its reactivity in the subsequent cycles, similarly to limestone.[9,13] By contrast, HA-85-850 was able to achieve a new, higher uptake upon each increase in carbonation time, and to retain it in the subsequent cycles, as clearly shown in Figure 3. However, these very extended carbonation times are unlikely to have industrial applicability.

Conclusions

The synthetic, Ca-based sorbent HA-85-850, containing 85 wt % CaO and 15 wt % $Ca_{12}Al_{14}O_{33}$, prepared by hydrolysis of CaO, showed a marked increase in its uptake of CO_2 when the inlet concentration of CO_2, y_{CO_2}, was increased during carbonation in a fluidized bed. By contrast, dolomite's uptake was independent of y_{CO_2}, similarly to limestone.

Furthermore, HA-85-850 showed a steady uptake of CO_2 uptake over a large number of cycles, and outperformed dolomite after 20 cycles. The uptake of both sorbents was found to increase with carbonation time: the increase was substantial for HA-85-850, but marginal for dolomite, as previously reported for limestone.[13] This unusual behavior of the synthetic sorbent HA-85-850 makes it an attractive solid for sequestering CO_2.

Acknowledgments

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