Role of precalcination and regeneration conditions on postcombustion CO$_2$ capture in the Ca-looping technology

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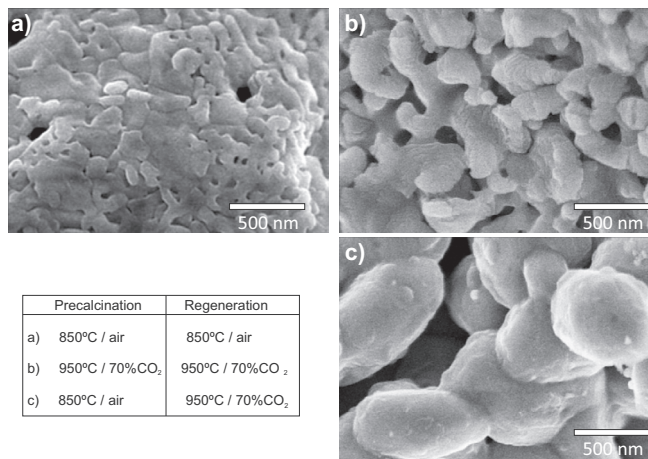[b] Instituto de Ciencia de Materiales de Sevilla (C.S.I.C. – Univ. Seville), Americo Vespucio 49, 41092 Sevilla, Spain

HIGHLIGHTS

- CO$_2$ capture performance of limestone at Ca-looping conditions is investigated.
- CaO is regenerated at high temperature and high CO$_2$%.
- Precalcination in air hinders CO$_2$ capture and causes particle fragmentation.
- Precalcination at high T/high CO$_2$% mitigates sorbent deactivation.
- Heat treatment and recarbonation enhance CO$_2$ capture if limestone is precalcined at high T/high CO$_2$%.

GRAPHICAL ABSTRACT

Limestone samples after 20 carbonation/regeneration cycles.

	Precalcination	Regeneration
a)	850°C / air	850°C / air
b)	950°C / 70%CO$_2$	950°C / 70%CO$_2$
c)	850°C / air	950°C / 70%CO$_2$

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ABSTRACT

The Ca-looping (CaL) technology is already recognized as a potentially viable method to capture CO$_2$ from postcombustion gas in coal fired power plants. In this process, CO$_2$ is chemisorbed by CaO solid particles derived from precalcination of cheap and widely available natural limestone. The partially carbonated solids are regenerated by calcination under high CO$_2$ concentration. Novel CaL concepts are proposed to further improve the efficiency of the technology such as the introduction of a recarbonation reactor in between the carbonation and calcination stages to mitigate the progressive deactivation of the regenerated CaO. Process simulations aimed at retrieving optimum design parameters and operating conditions to scale-up the technology yield results critically dependent on the multicyclic sorbent performance. Nevertheless, technical limitations usually preclude lab-scale tests from mimicking realistic CaL conditions necessarily involving high CO$_2$ concentration for sorbent regeneration and quick transitions between carbonation and calcination. In this work, a lab-scale experimental analysis is reported on the CaO multicyclic conversion at CaL conditions closely resembling those to be expected in practice. The results presented evidence a relevant role of precalcination conditions. Precalcination in air leads to a strongly adverse effect on the activity of the sorbent regenerated under high CO$_2$ concentration, which is further hindered if a recarbonation stage is introduced. On the other hand, sorbent deactivation is mitigated if precalcination is carried out at conditions similar to those used for sorbent regeneration. In this case, recarbonation helps lessening the loss of multicyclic conversion, which is further enhanced by the

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synergistic combination with heat pretreatment. Moreover, the present study shows that the kinetics of carbonation is strongly dependent on precalcination and regeneration conditions. The diffusion controlled carbonation phase and recarbonation are intensified if the sorbent is precalcined and regenerated under high CO_2 concentration whereas the reaction controlled carbonation phase is notably hampered.

1. Introduction

The Ca-looping (CaL) technology has recently emerged as a potentially feasible method for postcombustion CO_2 capture in coal fired power plants [1–3]. The process is based on the multicyclic carbonation/calcination of CaO. CO_2 present in the high velocity postcombustion gas stream (in a concentration of around 15% vol.) is captured by carbonation on the surface of CaO particles in a fluidized bed reactor (carbonator) operated at temperatures around 650 °C under atmospheric pressure. This temperature ensures a sufficiently low value of the equilibrium CO_2 concentration ($\simeq 1\%$ [4]) and, at the same time, a quick enough reaction kinetics for carbonation to occur in short residence times to considerably reduce the CO_2 concentration of the gas exiting the carbonator. The partially carbonated particles are then circulated into a second reactor (calciner) in which CaO is regenerated by calcination at high temperature while a stream of highly concentrated CO_2 gas exits the calciner ready to be compressed and transported. A critical issue of the technology is that the sorbent must be necessarily regenerated in the calciner under high CO_2 concentration (typically between 70% and 90% vol.), which requires raising up the temperature in this reactor to a value close to 950 °C in order to achieve complete decarbonation in short residence times [3,5–8]. The most feasible method to attain such high temperatures is to burn fuel in the calciner with pure oxygen (oxycombustion) for avoiding CO_2 dilution [3].

A main advantage to ensure the industrial competitiveness of the CaL technology is the low cost and wide availability of natural limestone to be employed as CaO precursor [9,10]. However, the multicyclic conversion of CaO derived from natural limestone decays progressively with the carbonation/calcination cycle number [11]. Lab-scale experiments show that the multicyclic conversion in short residence times of raw limestone derived CaO can be generally described by the semi-empirical equation [11–13]

$$\frac{X_N}{X_1} = \frac{X_r}{X_1} + \left[\frac{1}{k(N-1) + (1 - X_r/X_1)^{-1}} \right]; \quad (N = 1, 2 \ldots) \tag{1}$$

In Eq. (1), N is the cycle number, X_1 is CaO conversion in the 1st cycle, k is a deactivation constant and X_r is the so-called residual conversion, which is approached after a very large number of cycles. Most of data obtained for a diversity of natural limestones subjected to a wide diversity of conditions is reasonably well fitted by Eq. (1) using a residual conversion between 0.07 and 0.08 and a deactivation constant k close to 0.5 [12,14]. Conversion of CaO derived by limestone precalcination in air is very high. Thus, in the original derivation of Eq. (1) it was assumed $X_1 \approx 1$ [12]. On the other hand, it must be remarked that CaO regeneration in lab-scale tests is usually carried out by calcination under low CO_2 concentration.

A typical run in pilot plants to validate the CaL technology is initiated by precalcining a batch of limestone in air [3]. During this period, the net production of CO_2 in the calciner is only due to decarbonation of the initial inventory of limestone [3]. Once precalcination is finished, the calciner is started to operate in the oxycombustion mode, which raises its temperature and the CO_2 concentration to a high level for continuous operation. The calcined solids are taken to the carbonator after which they are

circulated back into the calciner wherein CaO regeneration would occur under high temperature/high CO_2 concentration. During continuous operation it is necessary to periodically feed the calciner with a make-up flow of fresh limestone to compensate for sorbent deactivation and loss of fine particles generated by attrition [3,15]. A major cause of process inefficiency is the large make up flow of fresh limestone required, which is somewhat compensated by the low cost of natural limestone and the possibility of using deactivated CaO for desulphurization and the cement industry [16,17]. Nevertheless, it is recognized that the excessively high consumption of fuel and oxygen used to raise the calciner temperature up to high enough values for complete calcination imposes an important energy penalty to the technology [18–20,6].

The introduction of a short recarbonation stage under high CO_2 concentration and high temperature in between the carbonator and the calciner is at the basis of a novel CaL concept aimed at minimizing the need of a large make up flow of fresh limestone to counteract sorbent deactivation [21–24]. The method is based on the recarbonation of the partially carbonated particles exiting the carbonator reactor using a high CO_2 concentration gas stream available from the calciner (see Fig. 1). Multicyclic carbonation/recarbonation/calcination thermogravimetric analysis (TGA) tests have already demonstrated that the residual conversion of raw limestone may be increased up to $X_r \simeq 0.16$ as compared to $X_r \simeq 0.07$ derived from ordinary carbonation/calcination cycles [21,25,23]. It is thus envisaged that the incorporation of a recarbonator reactor to the ordinary CaL process would serve to boost its efficiency by drastically reducing the required makeup flow of fresh limestone and hence the heat demand in the calciner thus lowering the overall cost of the CaL technology [21–23]. Based on these lab-scale results, a recarbonator reactor has been designed and the optimum operating conditions have been assessed [24] to validate the concept in an existing large-scale CaL pilot plant
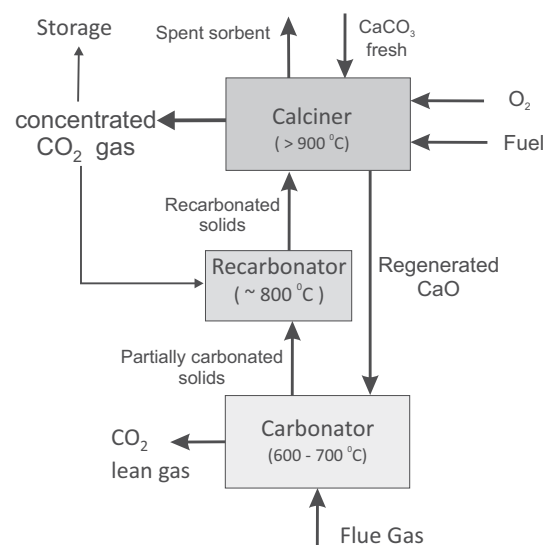

Fig. 1. Schematic representation of the Ca-looping process for post-combustion CO_2 capture modified by introducing a recarbonator reactor.