



## Research article

# Pressurized calcium looping in the presence of steam in a spout-fluidized-bed reactor with DFT analysis



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## ABSTRACT

Calcium looping is a high-temperature solid-looping process for CO<sub>2</sub> capture, exploiting cyclical carbonation of CaO. Previous work investigating the effects of steam on the carbonation reaction has produced conflicting results, with the majority of work conducted using thermogravimetric analyzers (TGA). Here, pressurized carbonation kinetics in the presence of steam in a 3 kW<sub>e</sub> pressurized spout-fluidized bed reactor, gives a rigorous insight into the effects of steam. Pseudo-intrinsic kinetics were determined using an effectiveness factor model along with activation energies and kinetic expressions. The mechanism in which steam promotes CO<sub>2</sub> adsorption on the surface of CaO was investigated using density functional theory (DFT). The molecular-scale changes on the CaO surface owing to the presence of steam compared to the base case of CO<sub>2</sub> adsorption on a ‘clean’ (without steam) surface were simulated with the Cambridge Serial Total Energy Package (CASTEP) software. The results suggest that steam promotes CO<sub>2</sub> adsorption via the formation of surface OH groups on the CaO surface.

## 1. Introduction

Calcium looping is a relatively new CO<sub>2</sub> capture technology which has been the subject of a great deal of attention and review [1–12]. The calcium looping cycle can be applied to various processes, such as electricity production in power stations, cement manufacturing, and iron and steel works [13,14]. There are a number of pilot-scale post-combustion projects currently being tested ranging from 1 MW<sub>th</sub> in Stuttgart, Germany to 1.9 MW<sub>th</sub> in Hualien, Taiwan. These facilities have demonstrated capture rates in excess of 85% and up to 1 ton of CO<sub>2</sub> capture per hour from cement plants and power stations [15–21]. Its use in pre-combustion capture combined with biomass gasification [22–24] and in situ capture combined with biomass combustion [25–28] for BECCS to achieve negative emissions has also shown promising results. Furthermore, there is potential for using the waste sorbent to capture additional CO<sub>2</sub> from the ocean through a process known as ocean liming [29,30] and reusing it as raw material for cement manufacture [31,32].

Two reactors are used in the looping process: One is the carbonator

(operating at temperatures around 650 °C and atmospheric pressures), in which the CaO sorbent reacts (reversibly) with the CO<sub>2</sub> present in flue gas to form CaCO<sub>3</sub>. The CaCO<sub>3</sub> is cycled to the second reactor (operating at around 900 °C under atmospheric pressures), where it decomposes back into CaO and a high-purity stream of CO<sub>2</sub>. The CO<sub>2</sub> stream is then purified, compressed and sent to storage.

Since one of the main components in the flue gas of power stations is steam, it is important to study the effects its presence has in the calcium looping cycle. Although there has been a significant volume of work published concerning the effects of steam on the calcination reaction [7,33–39], the effects of steam on the carbonation reaction has been reported in less detail. Although a few authors [37–42] have carried out experiments to examine its effects, the observations have not been in total agreement. Manovic and Anthony [40] found an improvement in rate when 10–20 vol% steam was present during the carbonation of seven types of limestone in a TGA. They also observed an improvement in the CaO conversion, particularly at the lower range of temperatures they investigated (350–600 °C) which they attributed to an enhancement in solid-state diffusion through the product layer. Donat et al. [41]

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reported a significant increase (more than double) in reactivity over 30 calcination/carbonation cycles when 10 vol% steam was used in a bench-scale atmospheric fluidized-bed reactor. Coppola et al. [37] reported a 22% increase in CO<sub>2</sub> capture capacity for the carbonation of Italian limestone in a fluidized-bed reactor. Contrastingly, Arias et al. [42] reported no improvement in the initial carbonation rate (kinetically-controlled step of carbonation) having carried out their experiments in a TGA under 20 vol% steam and 15 kPa of CO<sub>2</sub>.

The effect of steam on the carbonation reaction of Longcliffe limestone in a pressurized spout-fluidized-bed reactor has been investigated in this paper. Careful design of the experiments allowed the elimination of mass-transfer effects, which can be a significant effect in both TGA and fluidized bed work. The reactor allows high rates of heat and mass transfer to well-isolated individual particles, allowing accurate measurements of the intrinsic rate kinetics of carbonation. Furthermore, a large portion of the work provided here examines the effects of mildly pressurizing the process. Operating reactors at higher pressures may intensify the process by reducing the reactor size and therefore capital cost.

## 2. Material and methods

### 2.1. Materials

The calcium oxide particles required for this investigation were prepared from the ex situ calcination of naturally-sourced Longcliffe limestone (~98% purity CaCO<sub>3</sub> and sieved to known diameter ranges). For each batch of sample, 5 g of the limestone were weighed out, poured into a small hand-rolled tube of wire mesh and placed into a quartz liner (25.5 mm o.d., 543 mm L). The liner was heated inside a horizontal tube furnace (Lenton) at a rate of 60 °C min<sup>-1</sup> under a flow of nitrogen at 1.2 L min<sup>-1</sup> to a set-point of 850 °C. After maintaining isothermal conditions for 30 min at the set-point temperature, the sample was cooled down under the nitrogen and extracted at around 500 °C. The calcined sample was then held in a desiccator. Once the sample reached ambient temperature, it was transferred into a plastic vial and sealed with Parafilm M. This method was designed to maximize sample production rate and minimize its exposure to moisture since CaO is susceptible to hydration. Quality control of samples were carried out with a TGA (TA Instruments, QR5000 IR). The properties of the calcined samples are listed in Table 1.

The sand (G60 white silica sand) which was used as the inert fluidizing material for the spout-fluidized-bed reactor was supplied by David Ball Group PLC with a purity > 98%, and was sieved to a size fraction of 425–500 μm. The size fraction of sand was chosen to allow easy separation of the samples as well as maintain the fluidization characteristics of the bed. The potential to recover samples post-reaction is a significant advantage of this technology in comparison to smaller-scale reactors.

### 2.2. Experimental setup

The pressurized spout-fluidized-bed reactor (shown in Fig. 1) used

**Table 1**  
Properties of calcined Longcliffe limestone used in this investigation.

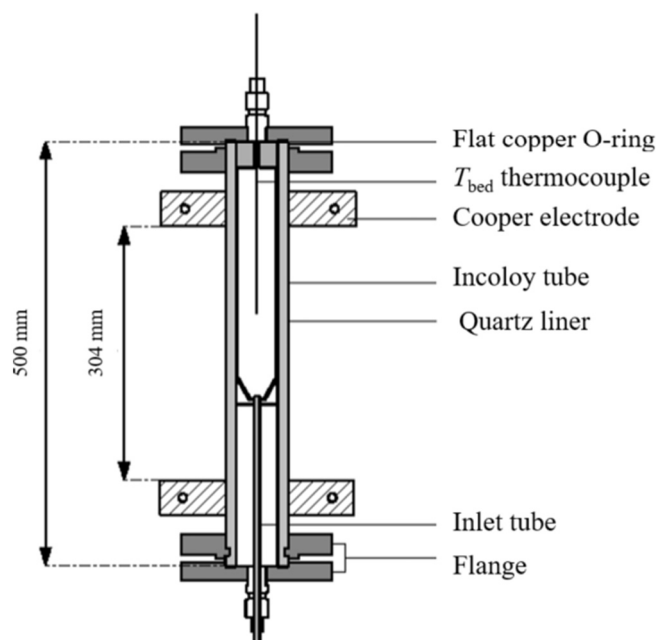
Degree of calcination (%)	BET surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Envelope density <sup>b</sup> (g m <sup>-3</sup> )	Skeletal density <sup>b,c</sup> (g m <sup>-3</sup> )	Porosity <sup>c,d</sup>
96.17 ± 0.87	19.40 ± 3.28	1.57 ± 0.05	3.15 ± 0.10	0.50 ± 0.01

<sup>a</sup> Measured using a nitrogen adsorption analyzer (Micromeritics, Tristar 3000).

<sup>b</sup> Measured with a helium pycnometer (Micromeritics, AccuPyc 1330).

<sup>c</sup> Measured with Mercury Intrusion Porosimetry (Micromeritics, Autopore IV).

<sup>d</sup> Porosity calculated for pore sizes < 10 μm to exclude interparticle spacing within the tested sample.



**Fig. 1.** Schematic diagram of the pressurized spout-fluidised-bed reactor (PSFBR).

in this investigation has been previously described by Zhang et al. [43] and used for kinetic measurements at low pressure. The reactor was a quartz liner (30 mm o.d., 260 mm L) with a 12.5 mm o.d. mouth at the bottom where the fluidizing gas entered. The liner was sealed within an Incoloy® Alloy 800HT cylindrical tube of 48 mm o.d. by a pair of flanges and a set of copper O-rings (FTI Ltd). The tube was resistance heated by a 3 kW<sub>e</sub> transformer via copper electrodes and was designed to withstand conditions up to 3 MPa and 1000 °C. K-type thermocouples were used to measure the temperature at the wall of the Incoloy tube and the temperature 10 cm above the mouth of the quartz liner (bed temperature).

Upstream of the reactor inlet was a solid feeding system which functioned in a similar fashion to a pressurized lock-hopper. The system consisted of a sample cylinder (to hold the sample prior to injection), a ball valve, a pressure gauge, a back-pressure regulator and a plug valve (large enough to allow solids to pass through smoothly). The ball valve controlled the direction of gas flow (either into the sample cylinder or bypassing it). The back-pressure regulator was used to pressurize the feeding section. The plug valve was positioned between the feeding section and the reactor and was only opened when injecting the solid sample into the reactor.

Downstream of the reactor was a condensation section, a solids filter, a pressure control valve (Bronkhorst), a moisture trap and a MGA3000C IR gas analyzer (ADC Gas Analysis). The condensation section was made of a 1" o.d. vertical stainless-steel tube immersed in a 2 L measuring cylinder which contained table salt, ice and water. Here, the steam was condensed out of the off gas from the reactor to avoid damaging the equipment downstream. The water was collected at the bottom of the cylinder and was removed using an air-locked stainless-steel drain. The solids filter (for elutriated particles) was a 1" o.d. horizontally-held stainless-steel tube packed with 6 g of glass wool (RS Components). A 0.5" o.d. horizontal stainless-steel moisture trap holding 8 g of CaCl<sub>2</sub> was situated in front of the inlet to the gas analyzer to remove residual moisture from the condensation section.

The steam generation system consisted of: a water tank, a Coriolis meter (Bronkhorst), a mass flow controller (MFC) supplied by Bronkhorst, a heating unit (Bronkhorst) and a humidity probe (Vaisala). The Coriolis meter was used to measure the mass flow rate of the water leaving the tank and entering the heating unit, and the MFC controlled the flow of the carrier gas (N<sub>2</sub>) which was used to deliver the water into

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