

# Reactivation of Limestone-Derived Sorbents using Hydration: Preliminary Results From a Fluidised Bed

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## Abstract

A simple method of CO<sub>2</sub> capture is by using the calcium looping cycle. The calcium looping cycle uses CaCO<sub>3</sub> as a CO<sub>2</sub> carrier, via the reversible reaction  $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons \text{CaCO}_{3(s)}$ , to extract CO<sub>2</sub> from the exhaust stream and provide a pure stream of CO<sub>2</sub> suitable for sequestration.

A problem associated with the technology is that the capacity of the sorbent to absorb CO<sub>2</sub> reduces significantly with the number of cycles of carbonation and calcination. The energy penalty of the cycle is considerably increased by cycling unreacted sorbent: hydration of unreactive sorbent has emerged as a promising strategy of reducing this penalty by regenerating the reactivity of exhausted sorbent.

A small atmospheric pressure fluidised bed reactor has been built and tested, that allows repeated cycling between two temperatures up to 1000 °C.

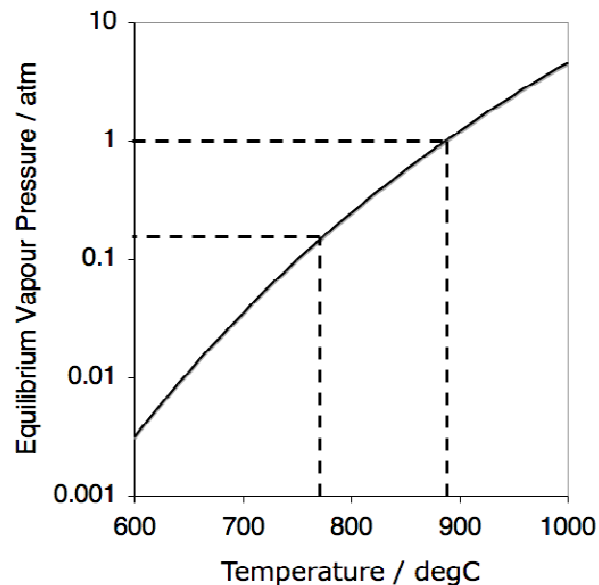
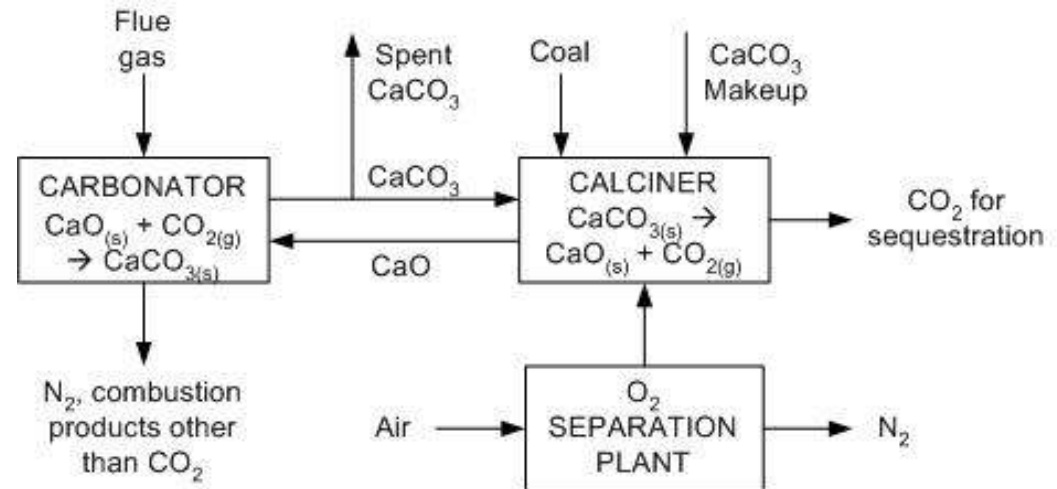
Work presented here focuses on the effects of variation of the calcination temperature before hydration. Hydration has been found to more than double the reactivity of a spent sorbent cycled under the mildest conditions studied (calcination temperature of 840 °C). However, as calcination temperature is increased the observed reactivation decreases until little reactivation is observed for the sorbent cycled at 950 °C. The primary reason for this appears to be a substantial increase in friability of particles, with reactivity normalised for mass losses appearing similar independent of cycling temperature.

# Calcium Looping

- Limestone is used as a reversible sorbent
  - Cheap and plentiful
  - Potential to sell on for cement manufacture
- Calcium looping centers around the reversible reaction
  - $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$
- Calcination step is the forwards step of this reaction
  - Endothermic process
  - Proceeds to completion over a wide range of conditions
- Carbonation is the backwards step
  - Exothermic process
  - Characterised by a fast initial rate followed by an abrupt transition to a very slow diffusion controlled reaction rate
  - It is only the fast initial reaction which is of interest for an industrial process
- Definition of carrying capacity:
  - Molar uptake of  $\text{CO}_2$  per one mole of CaO in sorbent (%) during the fast carbonation period

# Using the Calcium Looping Cycle

- A simple flow diagram for a post combustion carbon capture process harnessing calcium looping is shown
- The sorbent is continually cycled between the carbonator and calciner and acts as a CO<sub>2</sub> carrier, taking CO<sub>2</sub> from a stream of gas of a relatively low ppCO<sub>2</sub> in the carbonator, providing a stream of a high ppCO<sub>2</sub> in the calciner



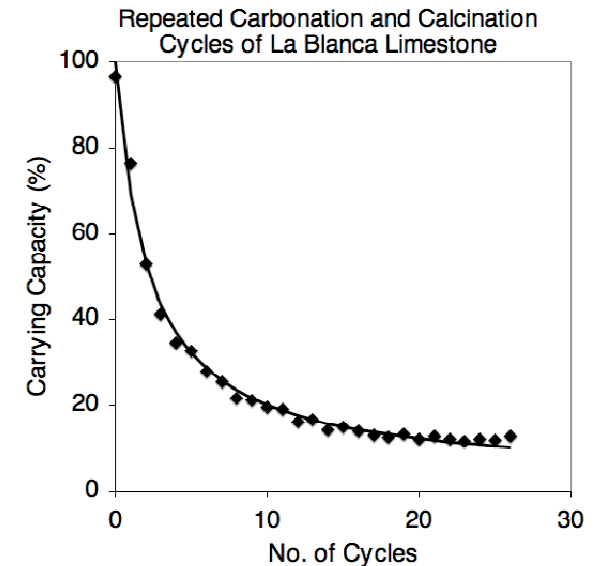
- The equilibrium vapour pressure for the reaction  $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons \text{CaCO}_{3(s)}$  is plotted
- For an atmospheric pressure process, the expected conditions are
  - ppCO<sub>2</sub> of 0.1 - 0.15 bar in the carbonator, necessary temperature of < 772 °C
  - ppCO<sub>2</sub> of > 0.9 bar in the calciner, necessary temperature of > 882 °C

# Sorbent Degradation

- As the sorbent is repeatedly cycled, its carrying capacity is found to decrease
- This is largely attributed to the loss of porosity associated with small pores (< 100 nm)
- Degradation is found to be more severe under more highly sintering calcination conditions - at higher temperatures, higher residence times, higher partial pressures of CO<sub>2</sub> and H<sub>2</sub>O
- Degradation can be modelled by an equation proposed by Grasa *et al.*

$$C_N = \left[ \frac{1}{(1/(1 - a_\infty)) + kN} + a_\infty \right] \times 100$$

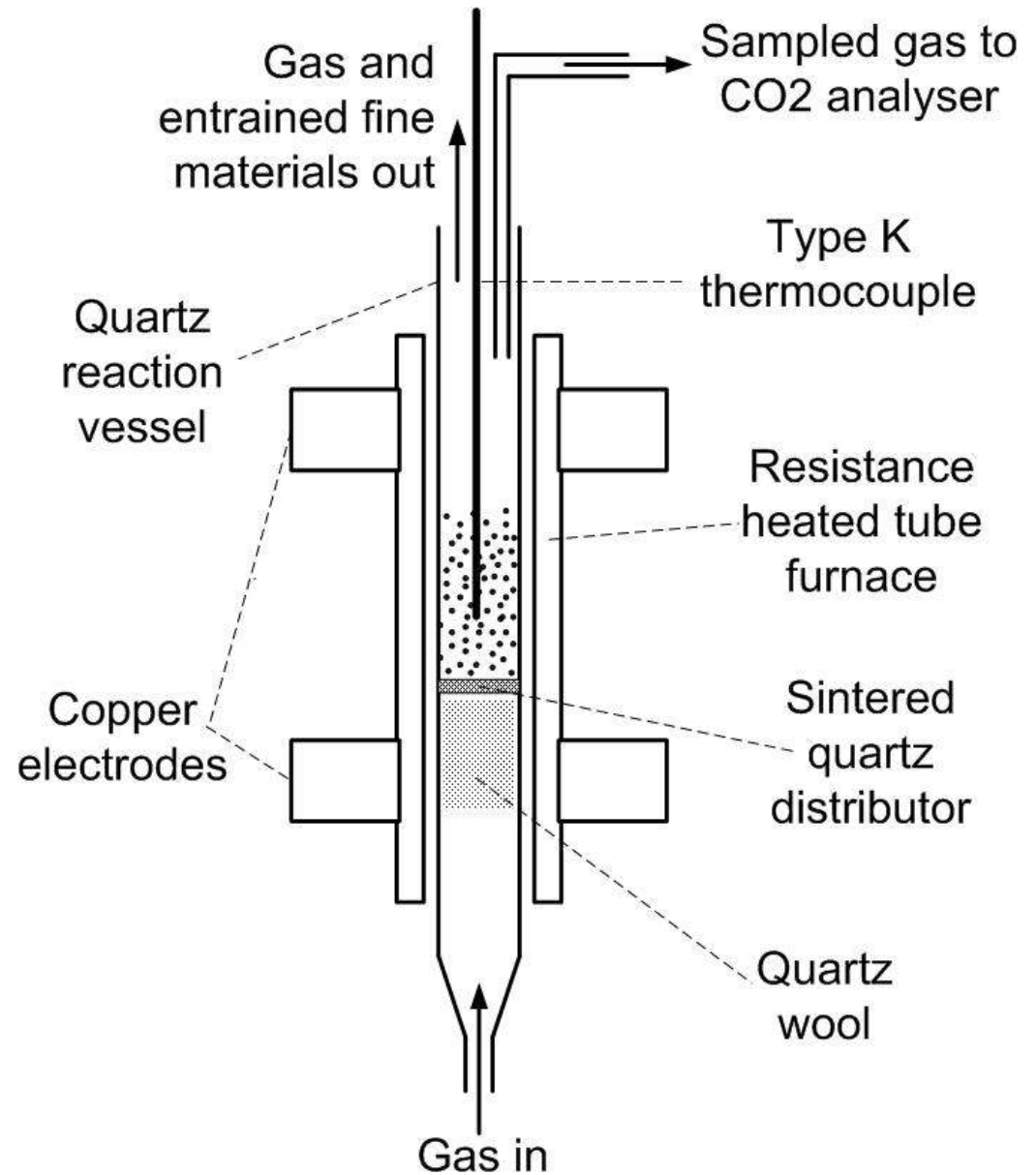
- $C_N$  is the carrying capacity in the Nth cycle
- $a_\infty$  is conversion at  $N = \infty$
- $k$  is a decay constant



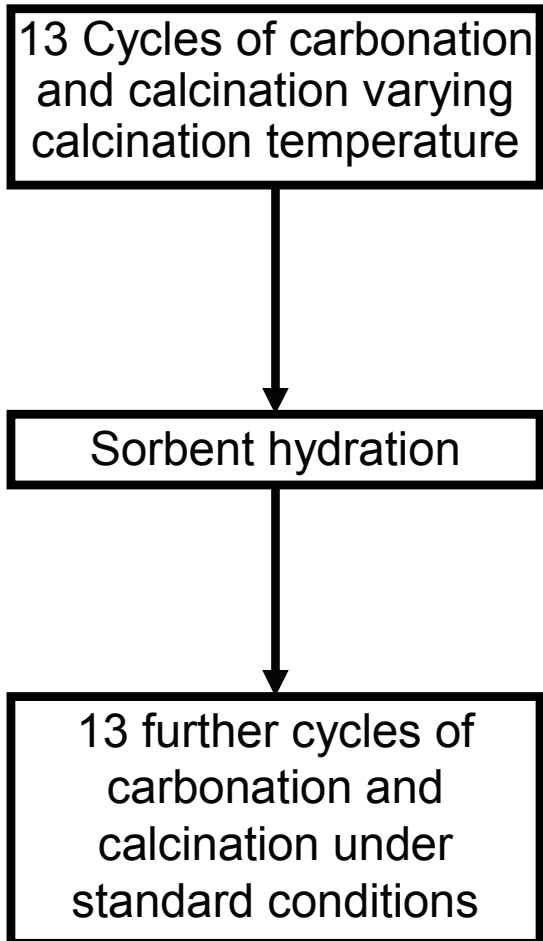
- This results in a large energy penalty associated with cycling large amounts of unreacted sorbent
- How can we reduce this penalty?
- Sorbents have been found to have an increased reactivity following hydration: less unreacted sorbent to be cycled
- Work so far has focused on TGA and low temperature fluidised bed environments: this project aims to look at more realistic conditions in a fluidised bed environment

# Fluidised Bed Reactor

- Designed, built and tested for this project
- Small fluidised bed (ID = 21 mm)
- Resistance heated furnace
- Temperature range of up to 1000 °C at ambient pressure
- Capable of cycling between two temperatures to allow carbonation and calcination within same vessel
- Gas and fines vented to atmosphere



## Experimental Work



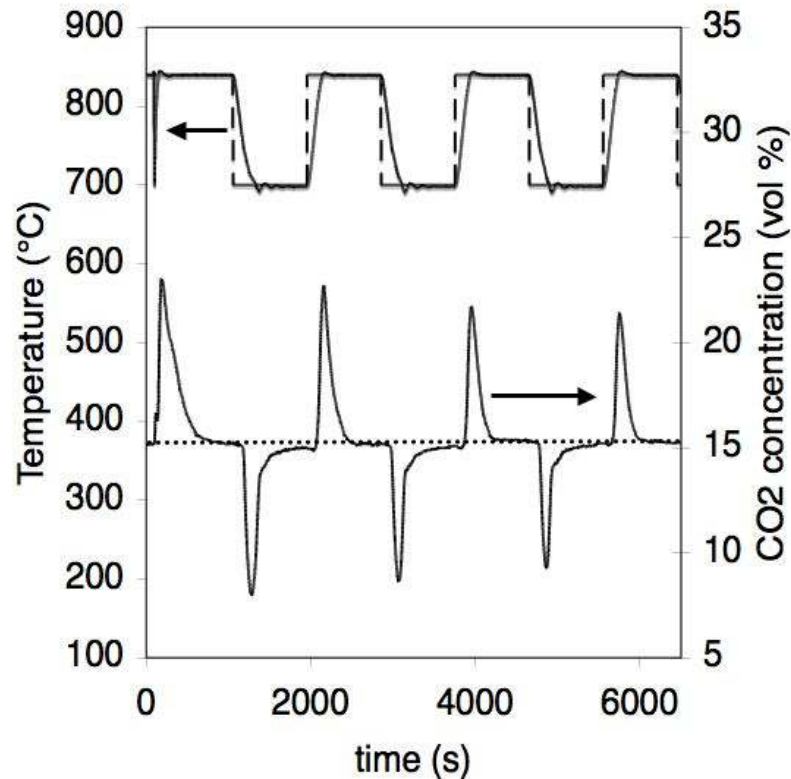
**Creation of spent sorbent:** Standard cycling experiments, but with variation of calcination temperature.  $T_{\text{calc}} = 840, 900, 950, 1000 \text{ } ^\circ\text{C}$

**Standard cycling experiments:** 15%  $\text{CO}_2$ , atmospheric pressure, 13 cycles of carbonation at  $700 \text{ } ^\circ\text{C}$  for 900 s and calcination at  $840 \text{ } ^\circ\text{C}$  for 900 s, 4.3 g Havelock limestone ( $500\text{-}710 \text{ }\mu\text{m}$ ) in 8 mL bed of sand ( $355\text{-}425 \text{ }\mu\text{m}$ ), flow rate  $\sim 8 U/U_{\text{mf}}$

**Hydration:** 38 hrs in a humidior at room temperature. Particles of Havelock limestone found to be fully hydrated under these conditions

**Mass measurements:** Sample is carefully weighed before and after each cycling experiment

## Results from a Typical Experiment

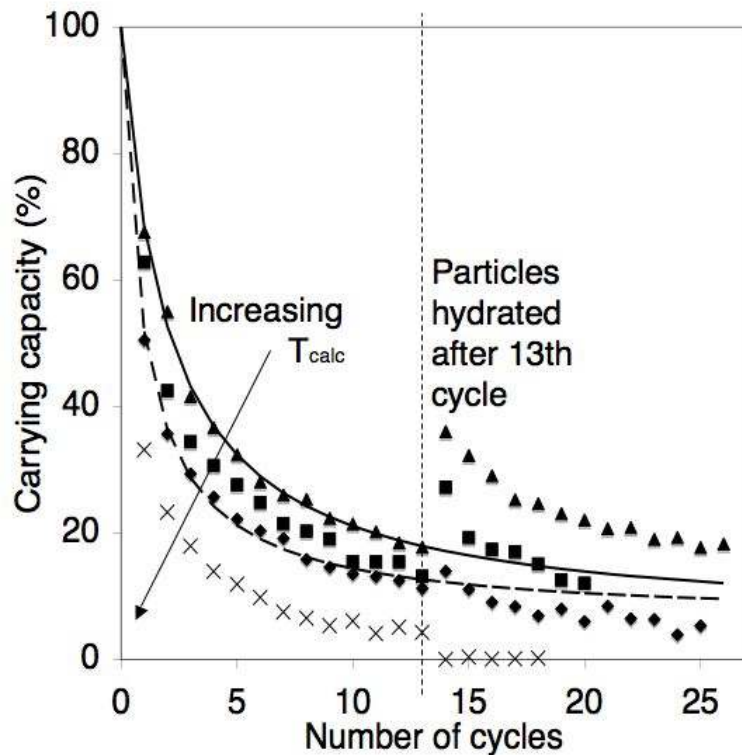


Temperature as function of time: bed temperature (—), temperature setpoint (---).  
CO<sub>2</sub> concentration as a function of time: outlet CO<sub>2</sub> concentration,  $X_{out}$  (—); inlet CO<sub>2</sub> concentration,  $X_{in}$  (···)

- Limestone added at 0 s whilst  $T = 840\text{ }^{\circ}\text{C}$  and particles calcine,  $X_{out}$  increases and a peak is observed before it returns to the value of  $X_{in}$  when calcination reaches completion
- After 900 s, setpoint is switched to  $T = 700\text{ }^{\circ}\text{C}$  and particles carbonate once a suitable temperature is reached,  $X_{out}$  decreases and a trough is observed - corresponding to the fast carbonation period - before tending towards  $X_{in}$  as the slow carbonation stages kicks in
- After 900 s, setpoint is switched back to the calcination temperature and the cycle continues
- The peaks become smaller as the number of cycles increases corresponding to the degradation of the sorbent
- Carrying capacity for each cycle is calculated as the mean of the molar uptake of CO<sub>2</sub> during carbonation and the molar emission from the following calcination divided by number of moles of CaO in the original sample



# Reactivation of Sorbents Cycled at Different Calcination Temperatures



Experimental data for  $T_{calc} = 840$  ( $\blacktriangle$ ),  $900$  ( $\blacksquare$ ),  $950$  ( $\blacklozenge$ ) and  $1000$  ( $\times$ ) °C, with fits of data to the Grasa Equation for the cycles before hydration of  $T_{calc} = 840$  (—) and  $950$  (---) °C

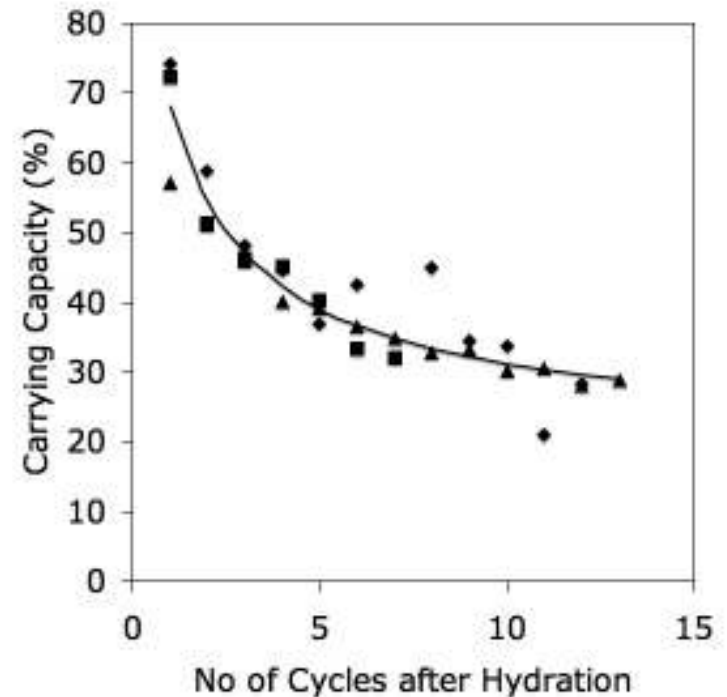
- Before hydration, deactivation rate of limestone is found to increase with increasing  $T_{calc}$ , as one would expect due to conditions becoming more highly sintering
- Limestone cycled with a calcination temperature of  $840$  °C undergoes the largest reactivation after hydration, with an observed doubling of carrying capacity
- As calcination temperature is increased, the reactivation extent is found to decrease
- The sample cycled at  $1000$  °C showed no reactivation: after hydration, peaks corresponding to calcination were found to be indecipherable to background noise on the analyser
- The efficacy of hydration as a reactivation strategy is found to be closely linked to the friability of the particles after hydration

# Analysis of Attrition

$T_{calc}$	$\Delta C$ (%)	$\Delta m$ (%)
840	110	36.7
900	89	62.3
950	15	81.1
1000	~ (-100)	94.4

- $\Delta m$  refers to the mass loss during the whole experiment and  $\Delta C$  refers to the increase in carrying capacity for the first cycle after hydration, when compared to projections from the Grasa equation as applied to the cycles before hydration
- The mass change before hydration was typically 10 % for each calcination temperature studied, so the most significant mass losses were found after hydration

- The results indicate that particles cycled using higher calcination temperatures show increased friability upon hydration
- When carrying capacity is normalised for mass loss during an experiment, similar deactivation curves are observed for each sample - experimental data shown for  $T_{calc} = 840$  ( $\blacktriangle$ ),  $900$  ( $\blacksquare$ ) and  $950$  ( $\blacklozenge$ )  $^{\circ}\text{C}$
- It is possible to conclude that: for particles large enough to remain within the bed, hydration has reactivated them to the same extent, independent of cycling conditions before hydration



## Conclusions

- A small fluidised bed reactor has been constructed which is capable of cycling between two temperatures
- Properties of “reactivated” limestone derived sorbent for CO<sub>2</sub> have been investigated
  - Sorbents cycled under milder conditions show a greater extent of reactivation
  - This is largely due to an decreased friability of the hydrated sorbent, as reactivity of the “reactivated” sorbents normalised for mass losses appear similar independent of cycling conditions before hydration