

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

Mr. John Blamey

Dr. Paul S. Fennell

Prof. Denis R. Dugwell

Funding: EPSRC

Abstract

A simple method of CO₂ capture is by using the calcium looping cycle. The calcium looping cycle uses CaCO₃ as a CO₂ carrier, via the reversible reaction $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons \text{CaCO}_{3(s)}$, to extract CO₂ from the exhaust stream and provide a pure stream of CO₂ suitable for sequestration.

A problem associated with the technology is that the capacity of the sorbent to absorb CO₂ 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.

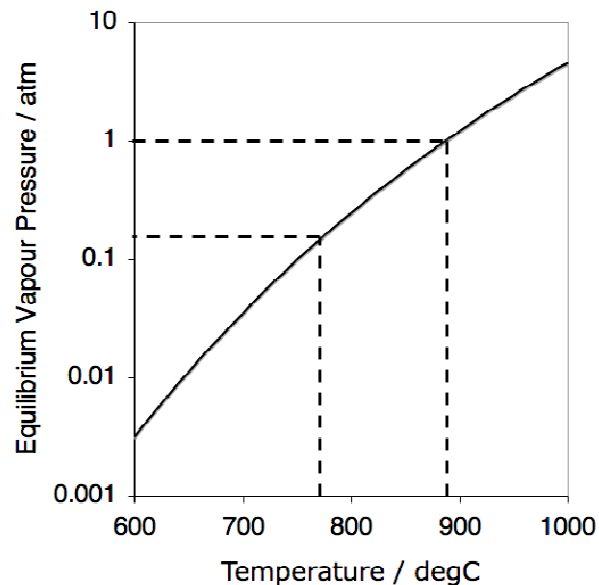
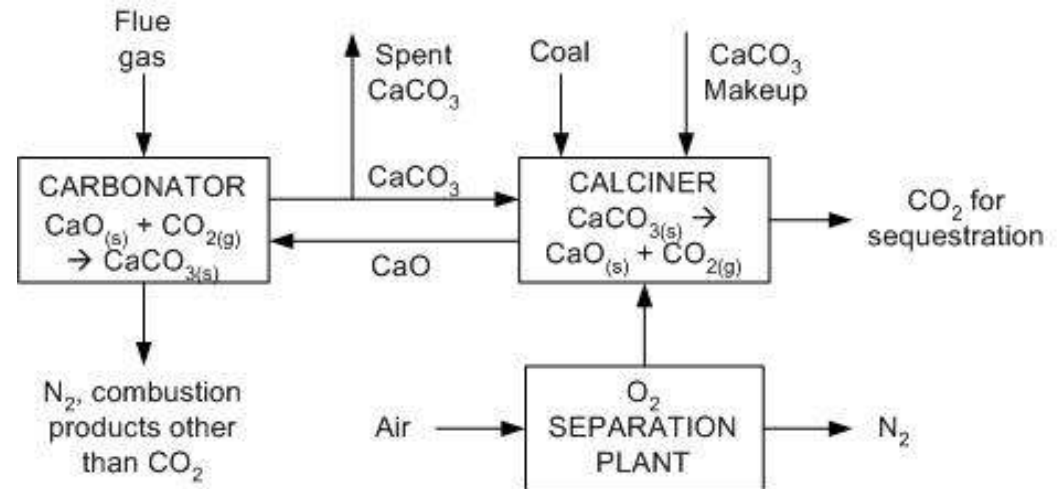
Work presented here focuses on the effects of variation of the calcination temperature before hydration. Hydration has been found to more than double the reactivity of a spent sorbent cycled under the mildest conditions studied (calcination temperature of 840 °C). However, as calcination temperature 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 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 CO₂ carrier, taking CO₂ from a stream of gas of a relatively low ppCO₂ in the carbonator, providing a stream of a high ppCO₂ in the calciner



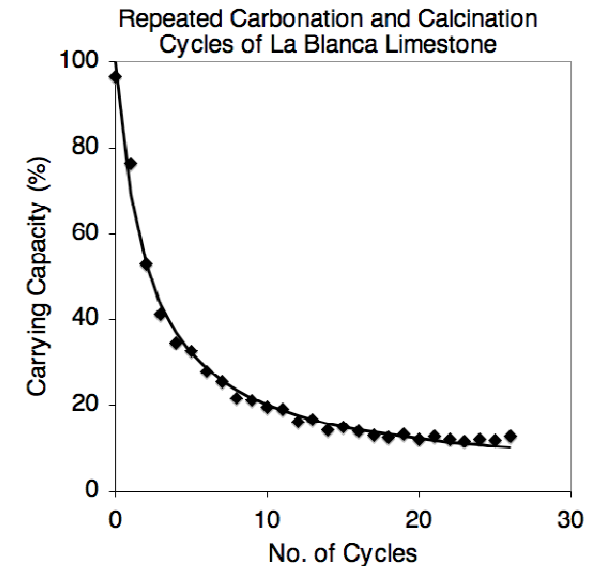
- The equilibrium vapour pressure for the reaction $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons \text{CaCO}_{3(s)}$ is plotted
- For an atmospheric pressure process, the expected conditions are
 - ppCO₂ of 0.1 - 0.15 bar in the carbonator, necessary temperature of < 772 °C
 - ppCO₂ of > 0.9 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 CO₂ and H₂O
- Degradation can be modelled by an equation proposed by Grasa *et al.*

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

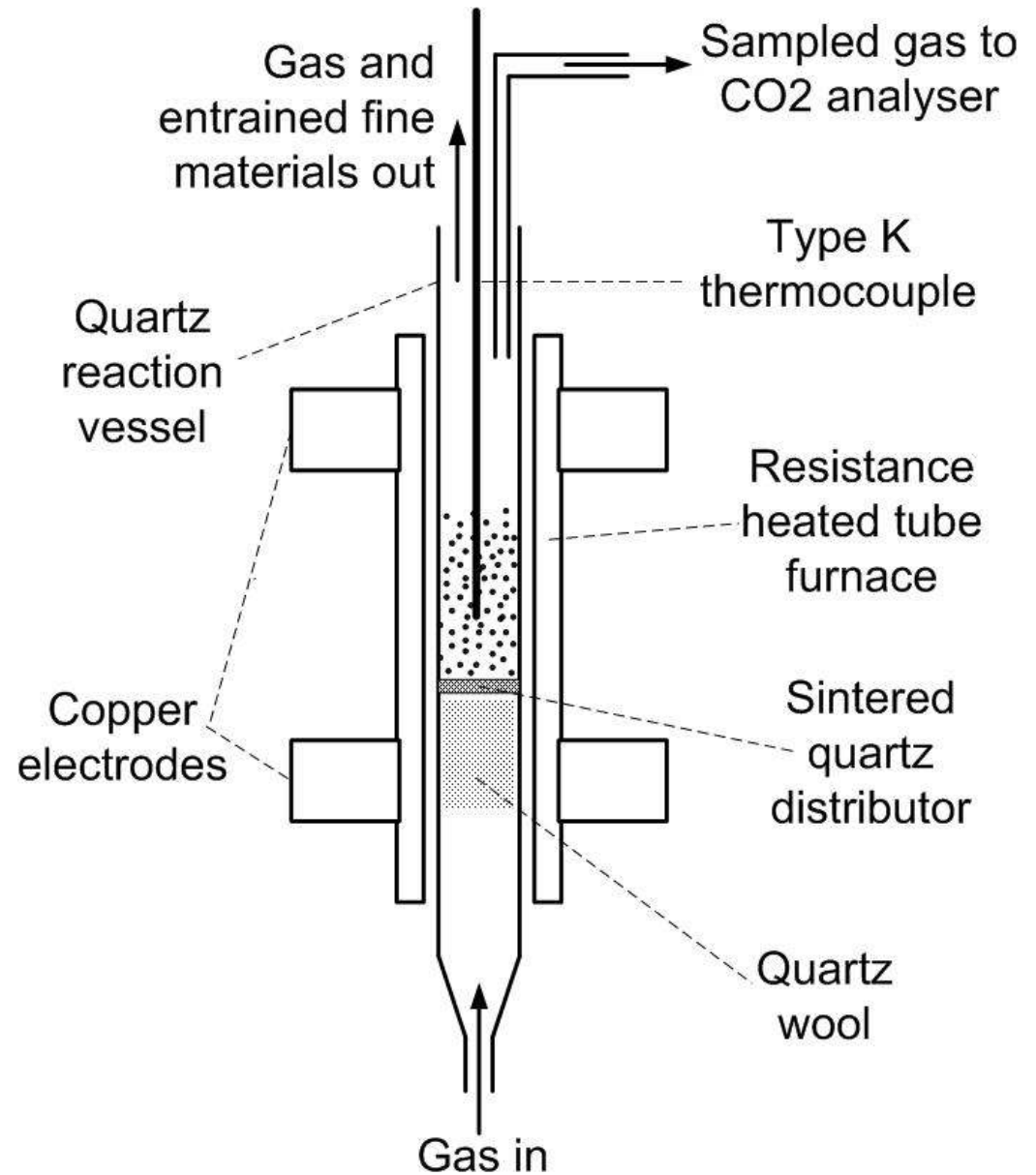
- C_N is the carrying capacity in the Nth cycle
- a_∞ is conversion at $N = \infty$
- k is a decay constant



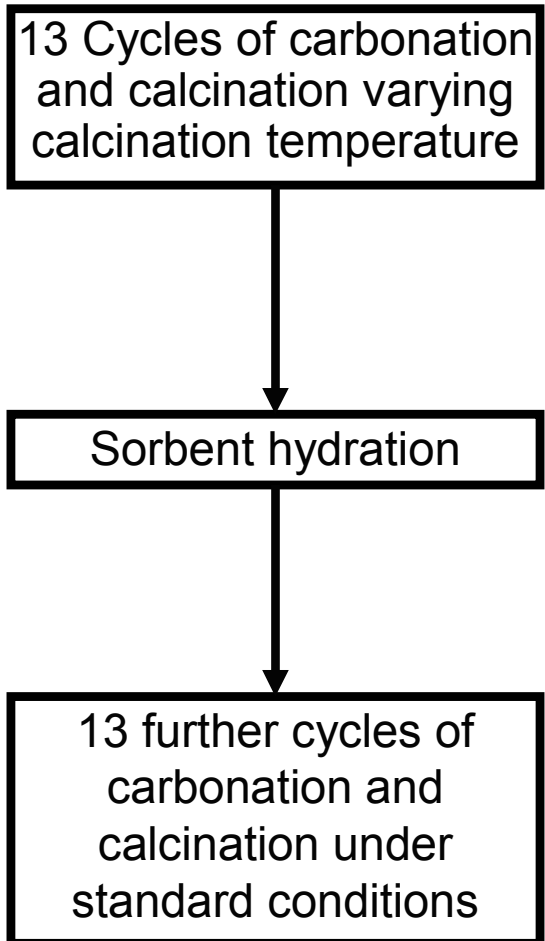
- This results in a large energy penalty associated with cycling large amounts of unreacted sorbent
- How can we reduce this penalty?
- Sorbents have been found to have an increased reactivity following hydration: less unreacted sorbent to be cycled
- Work so far has focused on TGA and low temperature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



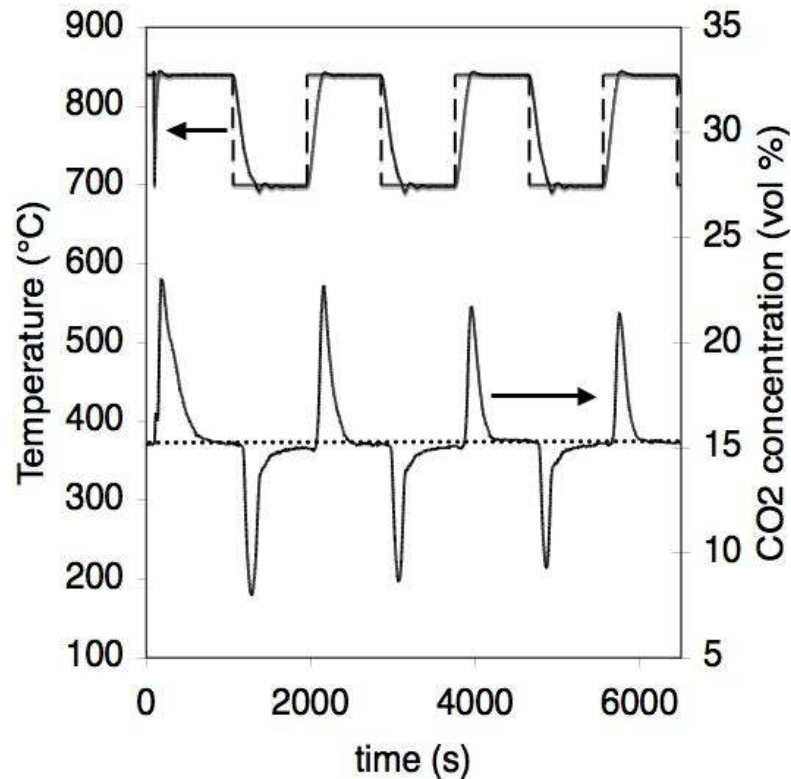
Creation of spent sorbent: Standard cycling experiments, but with variation of calcination temperature. $T_{\text{calc}} = 840, 900, 950, 1000 \text{ }^{\circ}\text{C}$

Standard cycling experiments: 15% 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 humidor 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

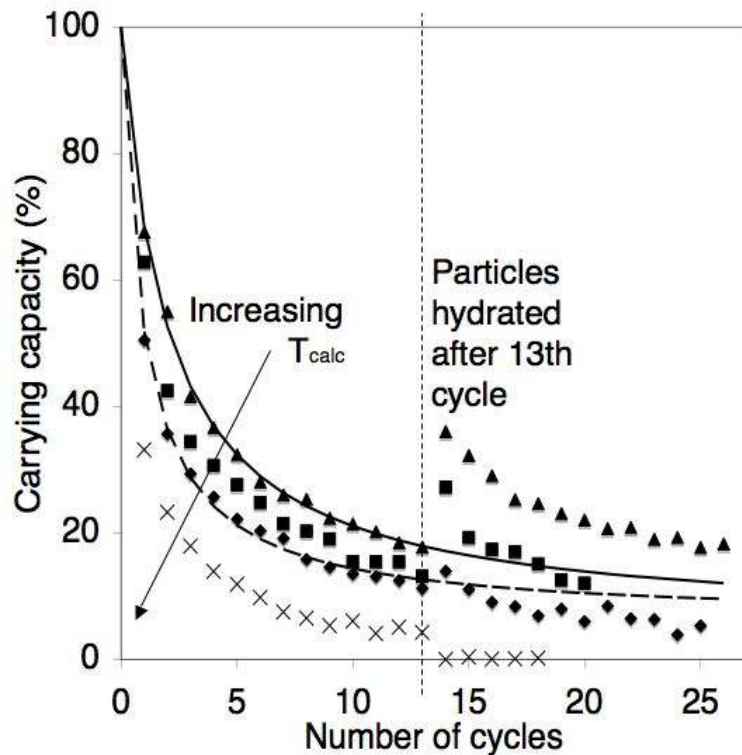
Results from a Typical Experiment



Temperature as function of time: bed temperature (—), temperature setpoint (---).
CO₂ concentration as a function of time: outlet CO₂ concentration, X_{out} (—); inlet CO₂ 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 CO₂ 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 $T_{calc} = 840$ (▲), 900 (◻), 950 (◆) and 1000 (×) °C, with fits of data to the Grasa Equation for the cycles before hydration of $T_{calc} = 840$ (—) and 950 (---) °C

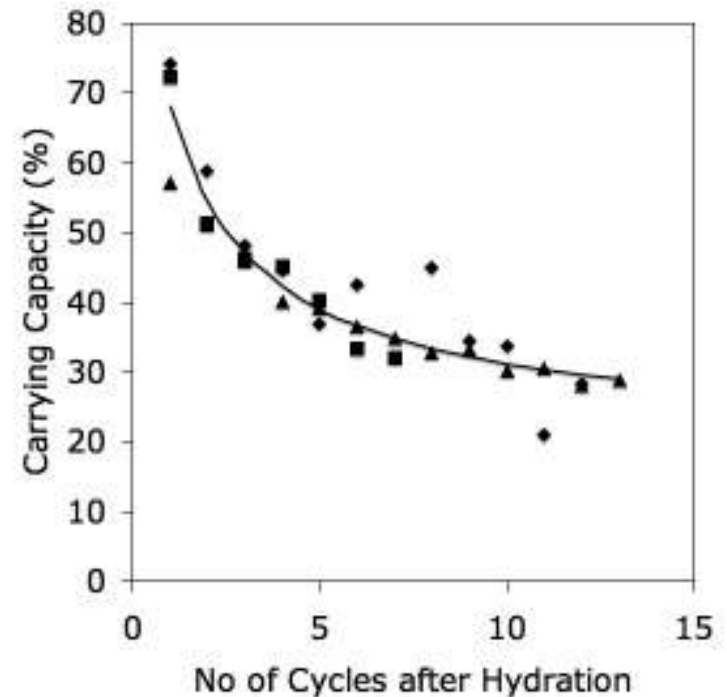
- Before hydration, deactivation rate of limestone is found to increase with increasing T_{calc} , as one would expect due to conditions becoming more highly sintering
- Limestone cycled with a calcination temperature of 840 °C undergoes the largest reactivation after hydration, with an observed doubling 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}	ΔC (%)	Δm (%)
840	110	36.7
900	89	62.3
950	15	81.1
1000	~ (-100)	94.4

- Δm refers to the mass loss during the whole experiment and ΔC 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) °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 CO₂ 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