



# Overview of CCS Research Activities



[www.imperial.ac.uk/ccs](http://www.imperial.ac.uk/ccs)

## Imperial College Centre for Carbon Capture and Storage

IC<sup>4</sup>S is a new Centre at Imperial formed under the auspices of the Energy Futures Lab.

It is a research network involving 30+ academic staff across several departments, aimed at:

- promoting collaborative CCS research within Imperial
- establishing an industrial consortium to fund and select research projects
- playing a leading role in the CCS debate by engaging with government departments, industry and NGOs

Director: Prof. Martin Trusler.

Deputy Directors: Dr Paul Fennell and Dr Tara LaForce

## Examples of Current Research

### Whole Systems Engineering:

- NERC-funded consortium project

### Carbon Capture Projects:

- Advanced Amine Processes
- Chemical Looping

### CO<sub>2</sub> Transport Projects:

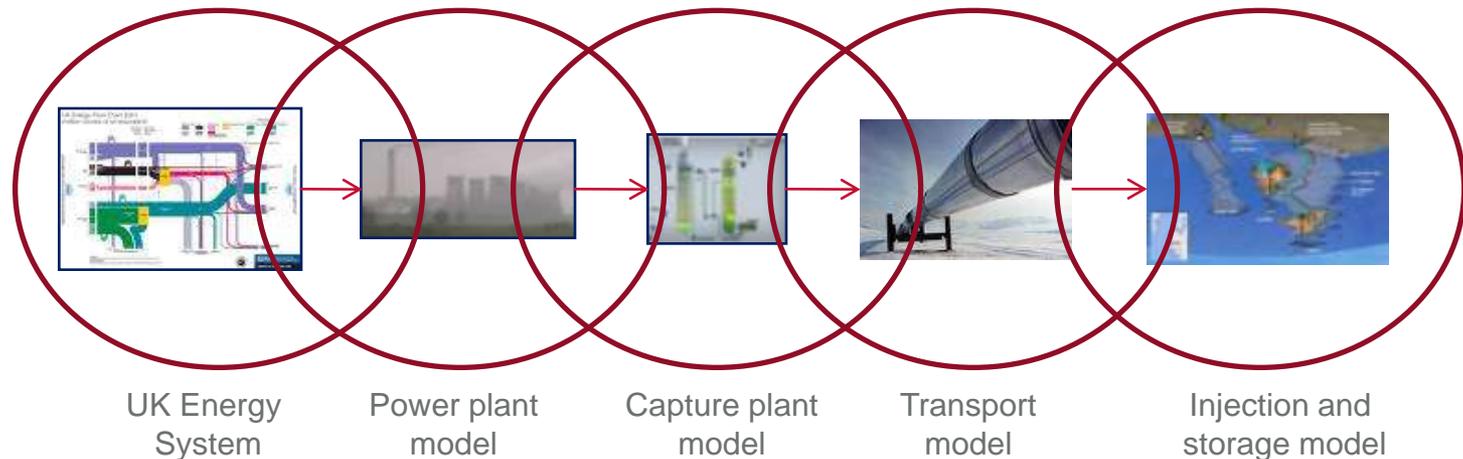
- EPSRC-funded consortium project

### Carbon Storage Projects:

- Shell/Qatar Petroleum-Supported Research Programme

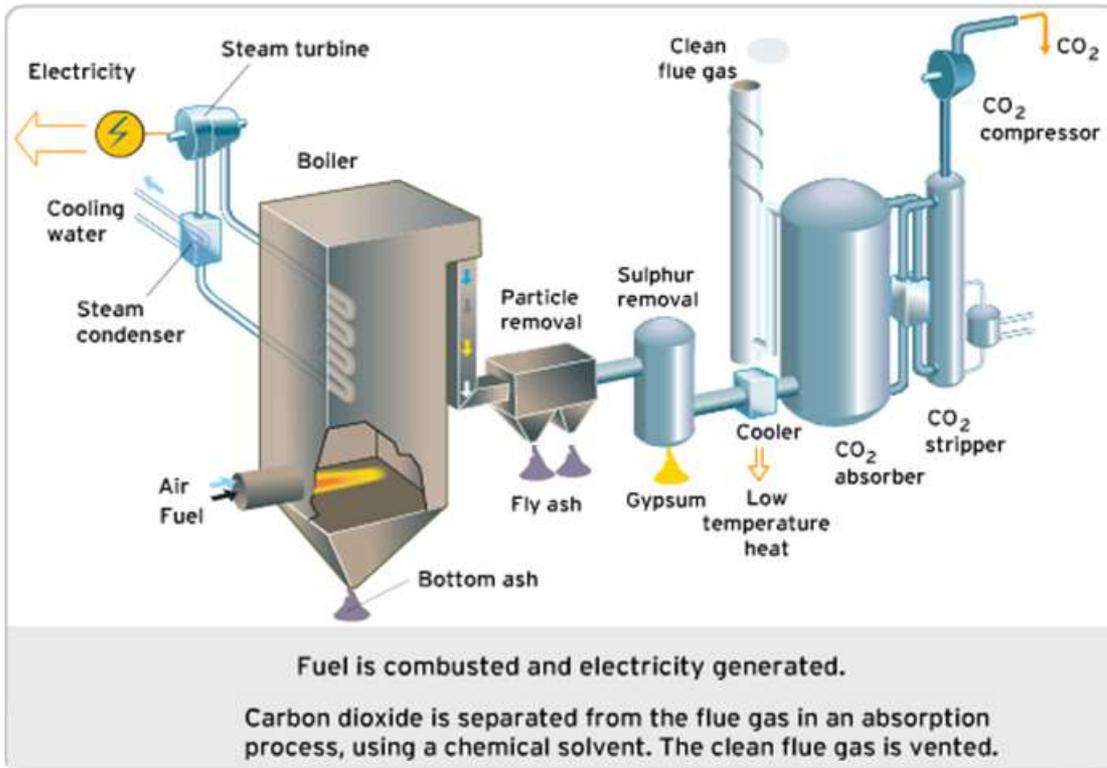
# Multiscale Whole Systems Modelling and Analysis for CO<sub>2</sub> Capture, Transport and Storage

- Consortium project involving Imperial, Cranfield University, Sussex University, British Geological Survey and multiple companies.
- Imperial PIs: Prof. Sevket Durucan and Prof. Nilay Shah.
- Objectives: to develop a systems modelling framework for CCS in the UK and apply this to quantify a series of environmental, economic and safety-related metrics



## Amine Capture Processes

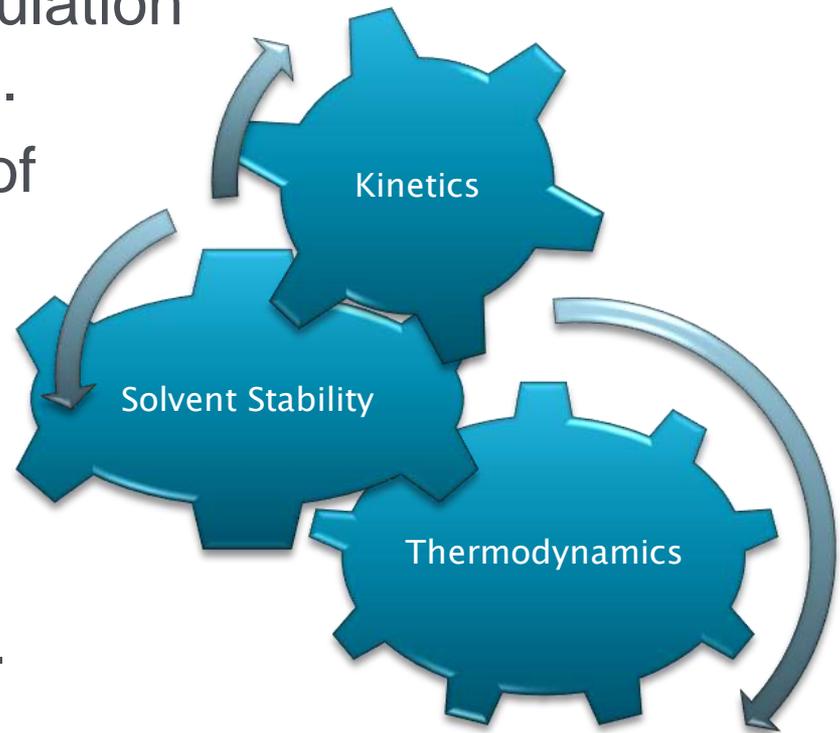
### The 'bolt-on' technology for post-combustion CO<sub>2</sub> capture



- Major cost penalties associated with amine processes need to be reduced.
- These breakdown roughly as follows:
  - CapEx: 33%
  - Energy: 56%
  - Other OpEx: 11%
- Energy costs are split ~50:50 between compression and solvent regeneration

## Solvent Design for CO<sub>2</sub> Capture From Flue Gas

- Development of advanced thermodynamic models to predict the solubility of CO<sub>2</sub> in liquid mixtures.
- Detailed thermodynamic and kinetic models for mixed physical and chemical solvents and their incorporation in advanced process design simulation tools, including solvent design.
- Experimental measurements of vapour-liquid equilibrium for new amine solvents.
- Investigation of corrosion effects, including enhanced solvent degradation due to metallic impurities such as Fe.



## Ca looping.

Research on the calcium looping cycle as a method of CO<sub>2</sub> capture

- Uses limestone - cheap and widely available - derived sorbent
- $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons \text{CaCO}_{3(s)}$
- Extract CO<sub>2</sub> from a gas of low ppCO<sub>2</sub>
- Providing gas stream of high ppCO<sub>2</sub>
- Decreasing reactivity of sorbent

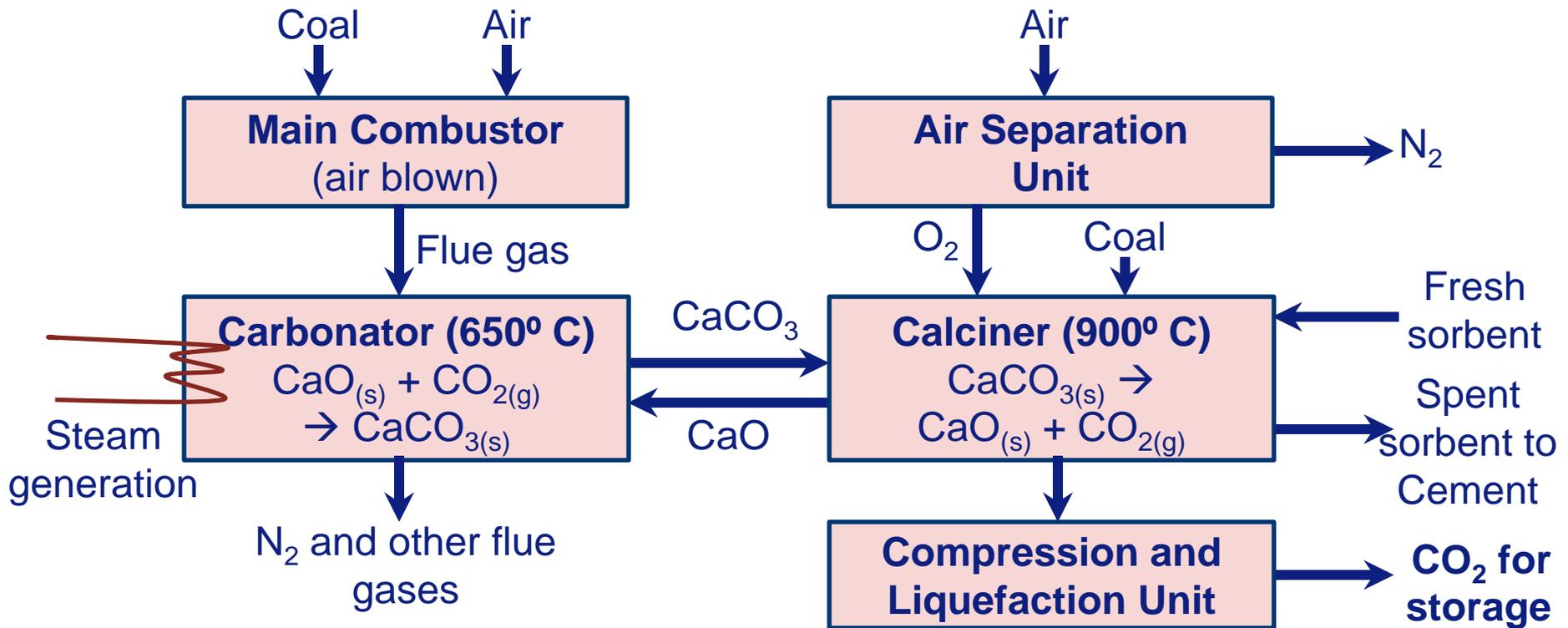
To study reactivation of 'spent' limestone based sorbents through hydration

- To characterise physical and chemical changes
- To optimise reactivation strategies

# The Basics of Calcium Looping

- Calcium looping centres around the reversible reaction
  - $\text{CaO}_{(s)} + \text{CO}_{2(g)} \rightleftharpoons \text{CaCO}_{3(s)}$
- 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 (%)

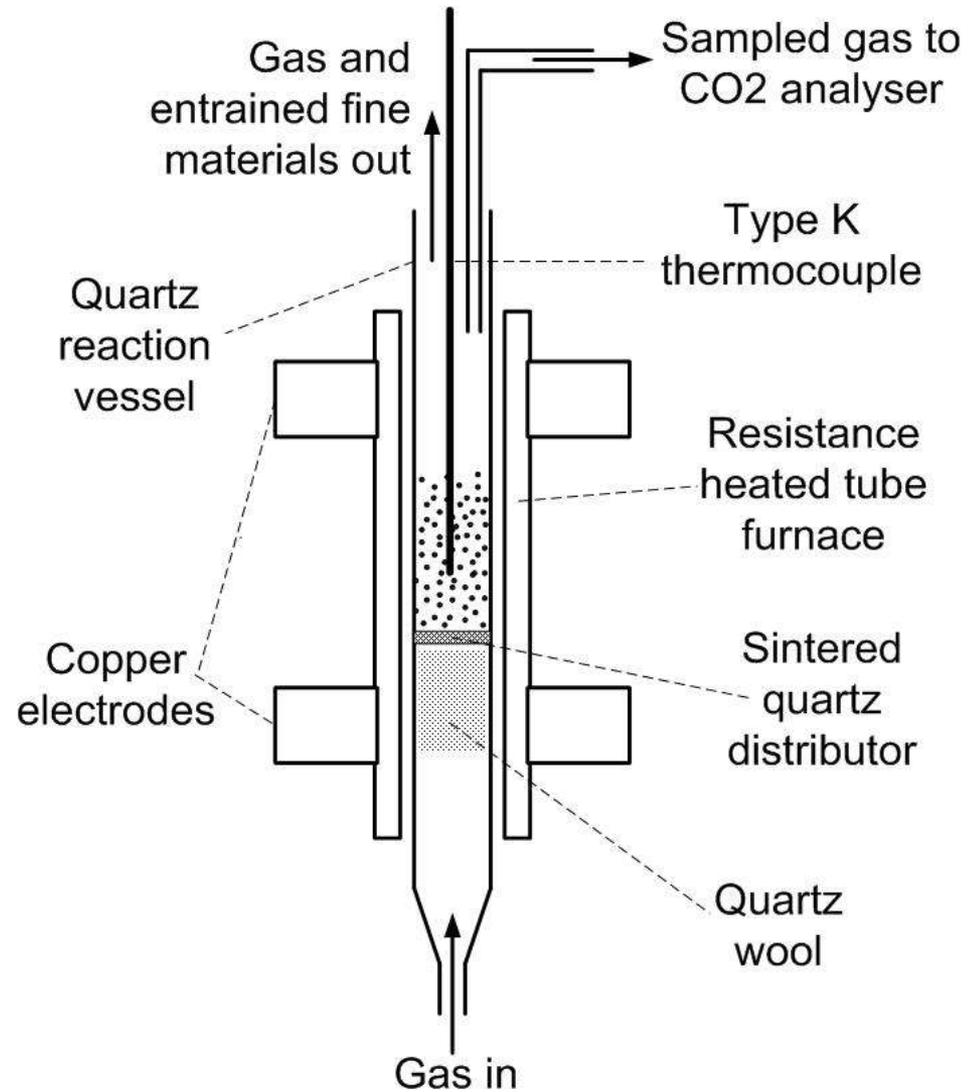
## Example Scheme for Post Combustion CO<sub>2</sub> Capture



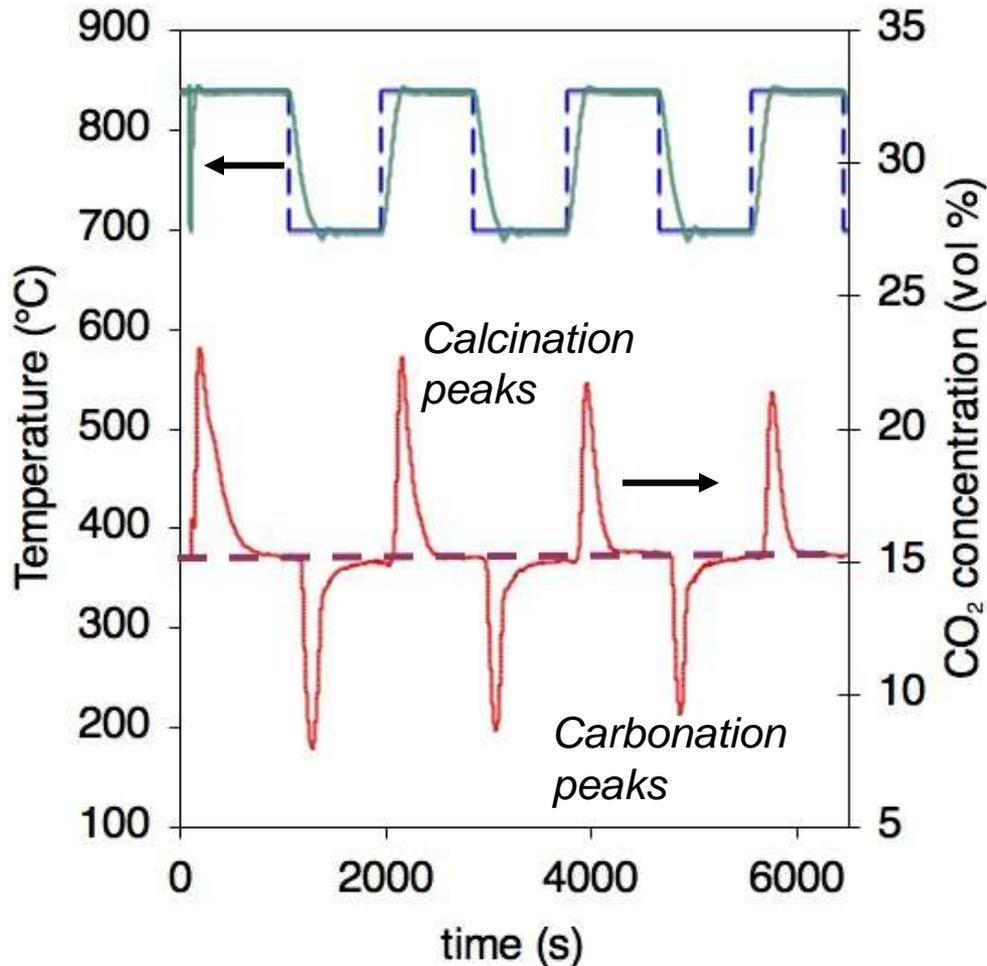
	Calcium Looping	Amine Scrubbing
Efficiency penalty (%)	6-8%	6-12%
Economics (Cost CO <sub>2</sub> avoided)	~ 20 USD/t	> 30 USD/t

## Design of 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



## Results from a Typical Experiment



Temperature as function of time: bed temperature (—), temperature setpoint (---).

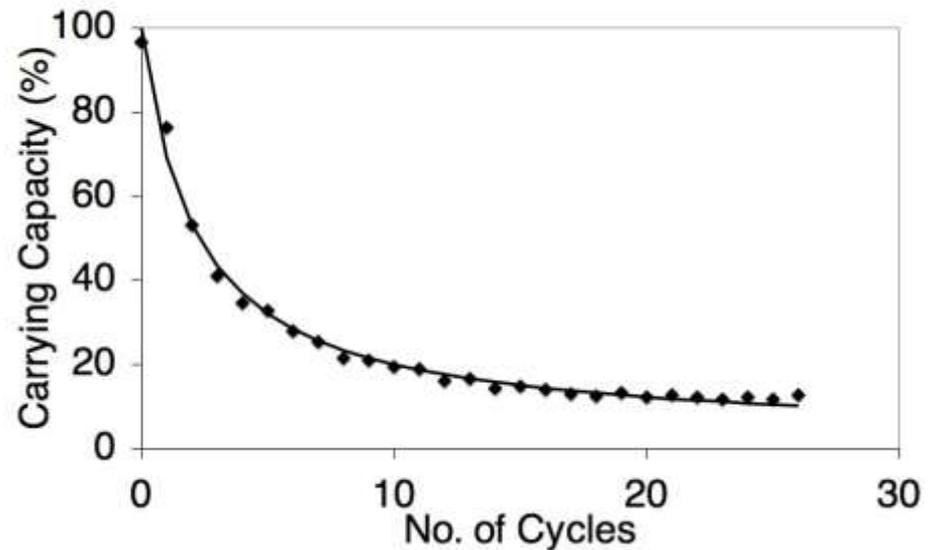
CO<sub>2</sub> concentration as a function of time: outlet CO<sub>2</sub> concentration,  $X_{out}$  (—); inlet CO<sub>2</sub> concentration,  $X_{in}$  (---)

## Extent of Carbonation

- After brief fast reaction period, reaction is diffusion controlled
- Carrying Capacity of sorbent found to decrease with no. of cycles
- Decay in molar uptake of CO<sub>2</sub> can be modeled 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

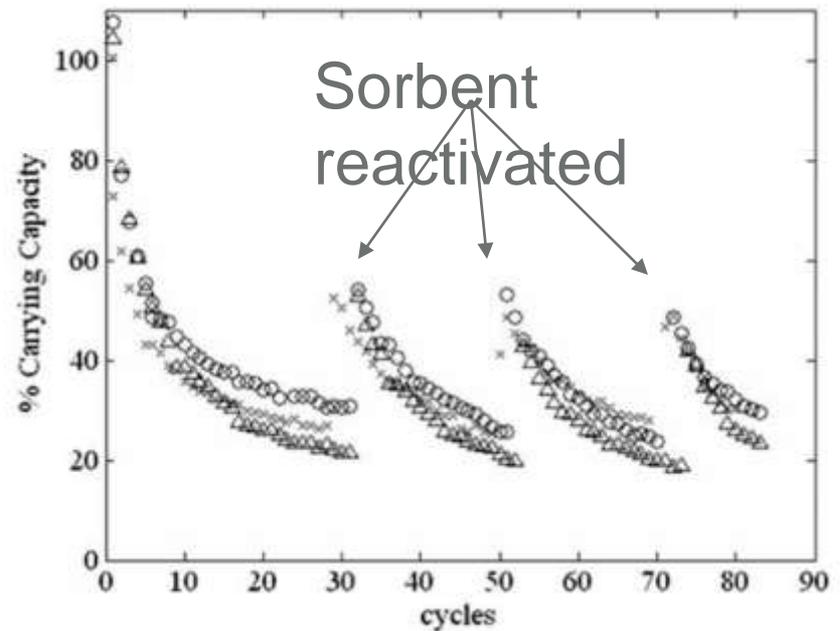


## Explaining the Loss in Reactivity

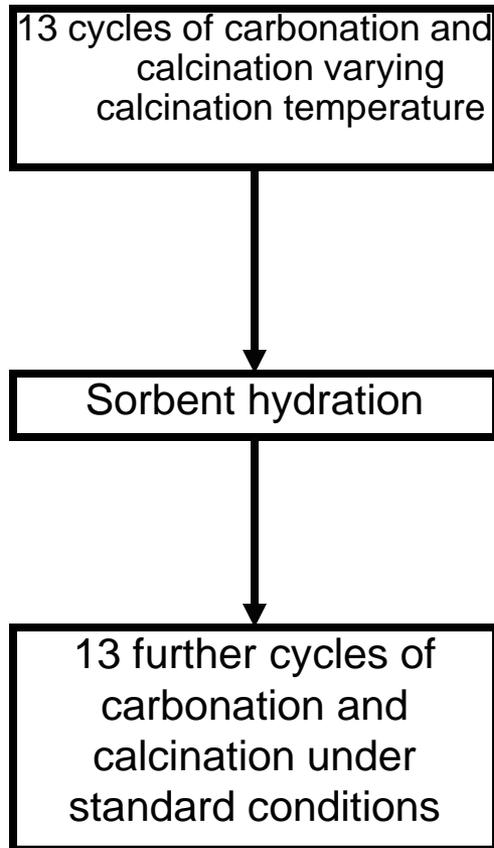
- Decrease in reactivity is attributed to changes in particle morphology
- Surface area and fraction of porosity associated with small pores (< 100 nm) found to decrease with number of cycles
- This is largely attributed to sintering in the calcination step
- Sintering has previously been found to increase at higher temperatures, concentrations of CO<sub>2</sub>, and time spent under these conditions - therefore sintering is a considerable problem under the conditions of the calciner (~ 950 °C and > 0.9 atm ppCO<sub>2</sub>)
- NOTE: There is further loss of reactivity of sorbent through competing sulphation reactions, ash fouling, and elutriation of attrited particles.

# Hydration

- If a calcined sorbent is hydrated, upon calcination an improved uptake of CO<sub>2</sub> can be observed
- Previous work has focused on TGA and low temperature fluidised bed environments
- Investigate reactivation of 'spent' sorbents using a small, bench scale, fluidised bed reactor
  - more realistic conditions than previously studied
  - potential to study attrition effects



## Experimental Work



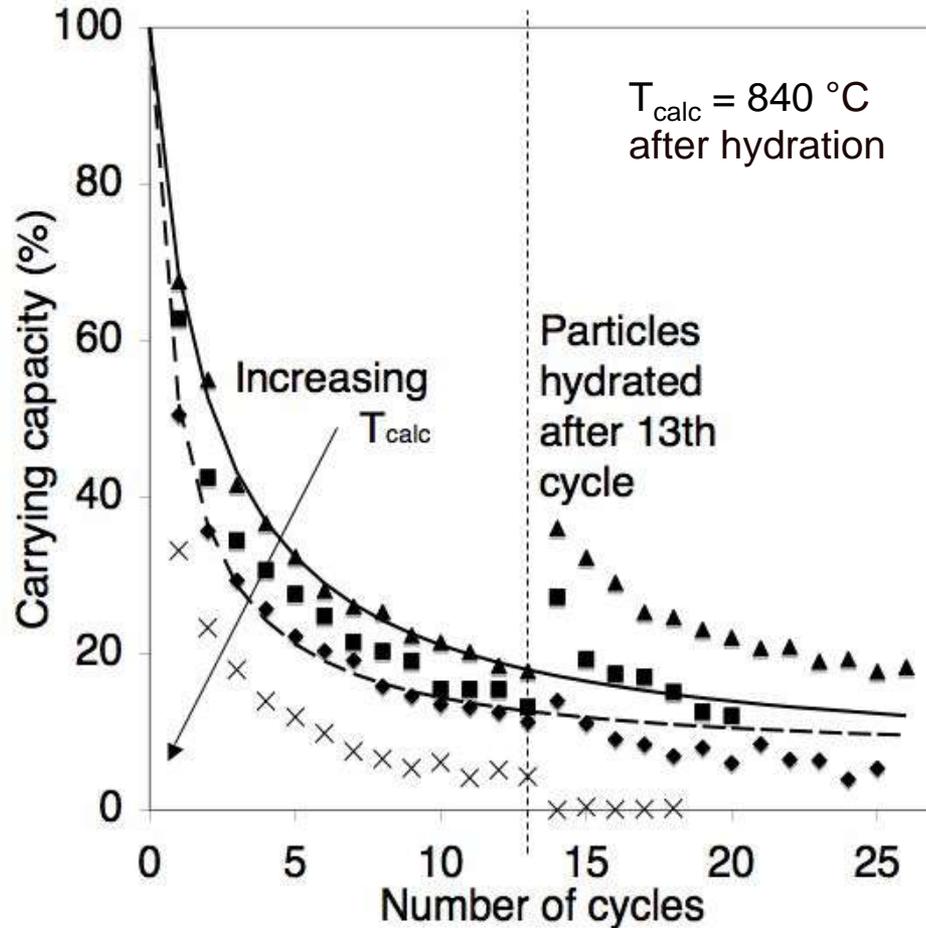
**Creation of spent sorbent:** Standard cycling experiments, but with variation of calcination temperature.  $T_{\text{calc}} = 840, 900, 950, 1000 \text{ }^{\circ}\text{C}$

**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  $\sim 8 \text{ U/U}_{\text{mf}}$

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

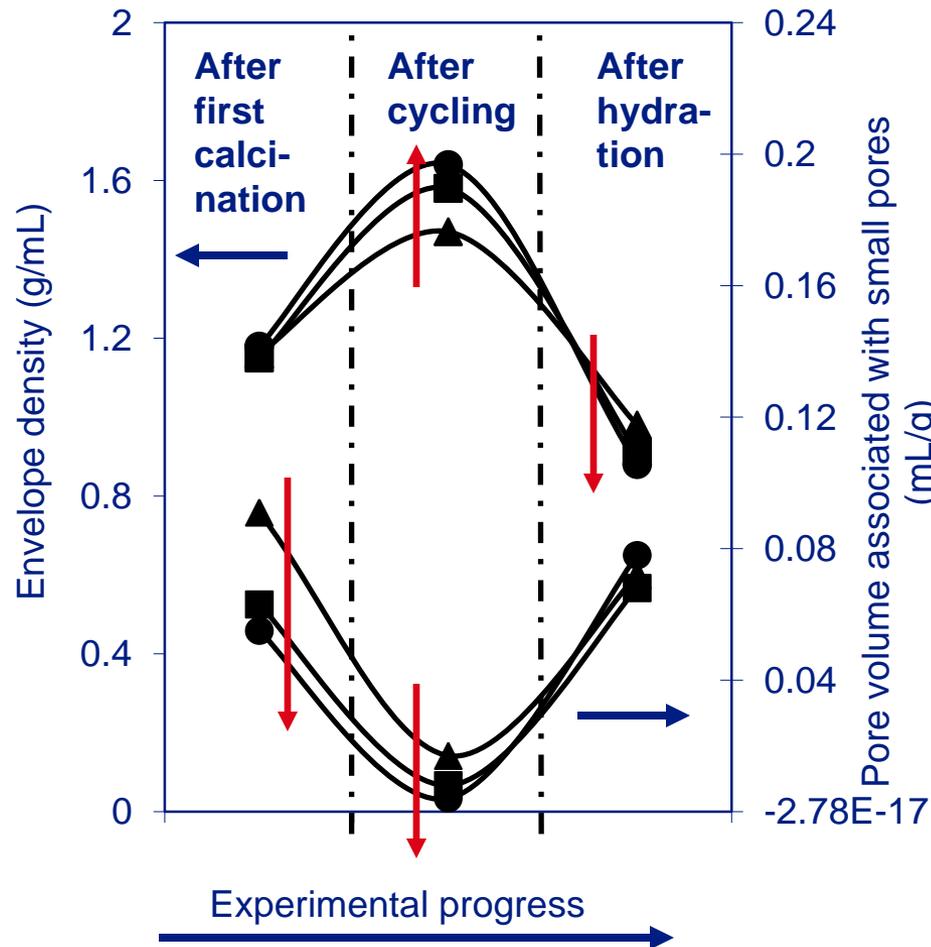
**Mass measurements:** Sample is carefully weighed before and after each cycling experiment

## Effect of Calcination Temperature Before Hydration



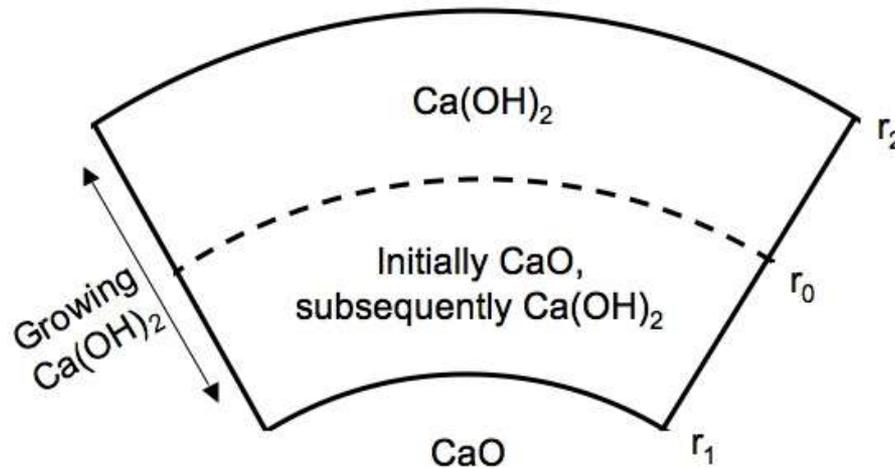
- Experimental data for  $T_{calc} = 840$  (▲),  $900$  (□),  $950$  (◆) and  $1000$  (×) °C
- Fits of data to the Grasa Equation for the cycles before hydration of  $T_{calc} = 840$  (—) and  $950$  (---) °C
- After hydration, all limestones are cycled under the same conditions

# Gas Adsorption and Density Analysis



- For Havelock limestone
- Separate experiments were ran for gas adsorption and density analysis: all results are for calcined samples
- $T_{\text{calc}} = 840$  (▲),  $900$  (◻),  $950$  (●)
- Pore volume associated with small pores decreases upon cycling and with increasing calcination temperature
- Pore volume increases after hydration, hence reactivation
- **Densification of particles is observed upon cycling and to be greater for samples cycled at higher values of  $T_{\text{calc}}$**
- Particles become considerably less dense after hydration: the least dense are the most friable

## Developing a Particle Break up Model



- A particle break up model is being developed based on a molar balance on the exterior of a particle during hydration
- The strain ( $\Delta r/r$ ) can be related to the stress,  $\sigma$ , by Hooke's law in an orthogonal coordinate system for an isotropic material, as described in Eq. (3)

Molar Balance:

$$\frac{4}{3} \pi (r_2^3 - r_1^3) \frac{\rho_{Ca(OH)_2} (1 - \varepsilon_{Ca(OH)_2})}{RMM_{Ca(OH)_2}} = \frac{4}{3} \pi (r_0^3 - r_1^3) \frac{\rho_{CaO} (1 - \varepsilon_{CaO})}{RMM_{CaO}} \quad \text{Eq. (1)}$$

$$X_C = 1 - \left( \frac{r_1}{r_0} \right)^3 \quad \text{Eq. (2)}$$

$$\frac{(1 - \nu)\sigma}{E} = \frac{\Delta r}{r} \quad \text{Eq. (3)}$$

## Particle Break Up Model

Outcome:

$$\sigma = \frac{E}{(1-\nu)} \left[ \alpha X_C + (1 - X_C)^{1/3} - 1 \right]$$

where:

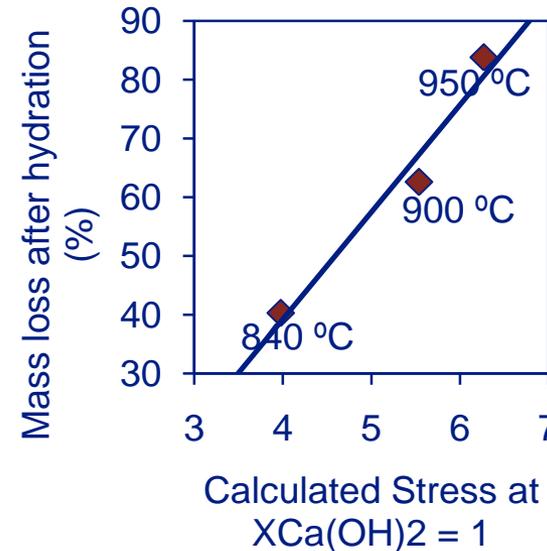
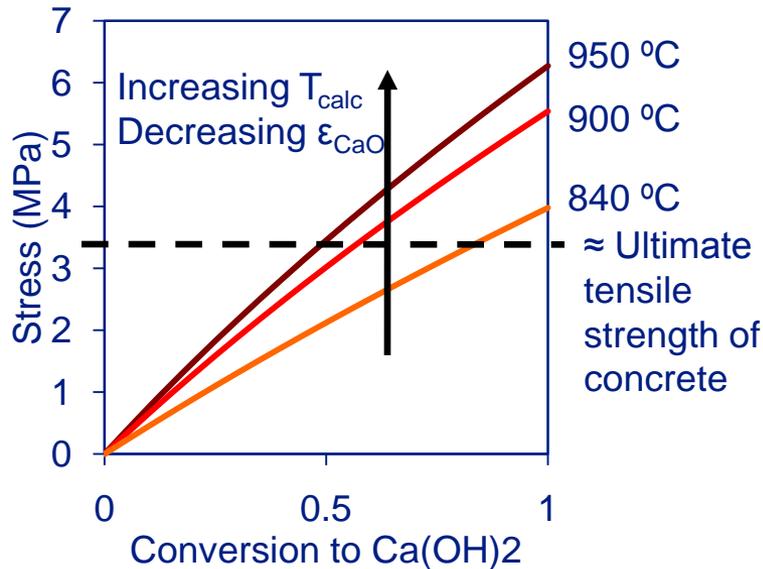
$$\alpha = \frac{\rho_{CaO} (1 - \varepsilon_{CaO}) RMM_{Ca(OH)_2}}{\rho_{Ca(OH)_2} (1 - \varepsilon_{Ca(OH)_2}) RMM_{CaO}}$$

NOTE:  $\varepsilon_{CaO}$  is shown to be less for samples cycled under more highly sintering environments (ie. higher calcination temperatures in this series of experiments)

# Particle Break Up Model Results

$$\sigma = \frac{E}{(1-\nu)} \left[ \alpha X_C + (1-X_C)^{1/3} - 1 \right]$$

$$\alpha = \frac{\rho_{CaO}(1-\varepsilon_{CaO})RMM_{Ca(OH)_2}}{\rho_{Ca(OH)_2}(1-\varepsilon_{Ca(OH)_2})RMM_{CaO}}$$



- Hence, we can plot the stress in the exterior of the particle as a function of conversion.
- If we know the ultimate tensile strength of particles, we should be able to predict whether – and at what conversion to hydroxide – particles of a specific porosity of calcium oxide producing a hydroxide of a specific porosity are going to fracture.
- We see a correlation between calculated stress at full conversion to Ca(OH)<sub>2</sub> and the extent of attrition after hydration

## Conclusions

While hydration has been proved to be an effective reactivation technique on a small fixed bed scale, it is less effective under fluidised conditions

The particles break up over hydration, producing much fine material, which is more likely to be entrained in the fluidised gas upon re-fluidisation

This is found to be more severe for samples that had been cycled at higher calcination temperatures

The reactivity of particles large enough to remain in the bed is found to remain constant, independent of cycling conditions before hydration

A particle breakage model is being developed to explain the increased likelihood of denser particles to fracture upon hydration

## Collaboration with CETC-O

- Collaboration has been initiated between the CANMET Energy and Technology Centre - Ottawa (CETC-O) in Canada and Imperial College, London
- Experimental work carried out at CETC-O
  - Two different limestones (Havelock & Katowice) were subjected to repeated cycles of carbonation and calcination under two different scenarios
    - » one in highly sintering calcination conditions
    - » one in mildly sintering calcination conditions
  - The experiments were carried out in both a TGA and a tube furnace
  - The objective of the work was to compare physical changes of the limestones
- SEM-EDX analysis was carried out in CETC-O
- Nitrogen adsorption analysis and pycnometry analysis carried out at Imperial College (discussed here)

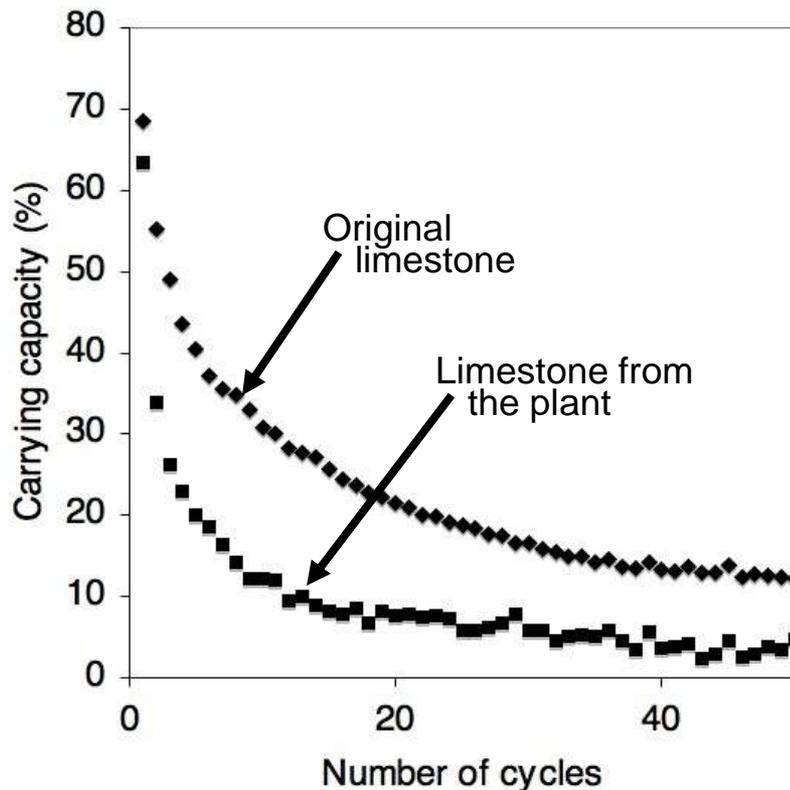
## Collaboration with CETC-0

Sample ID	BJH total volume of small pores [cm <sup>3</sup> /g]	Envelope Density [g / cm <sup>3</sup> ]
HV-cal-mild	0.223	1.08
HV-cyc-mild	0.109	1.20
HV-cal-harsh	0.069	1.24
HV-cyc-harsh	0.016	1.65

- HV – Havelock limestone
- cal – sample after the 1 calcination, cyc – sample after 10 cycles
- harsh – calcination(s) in 100% CO<sub>2</sub> with higher T, mild – calcination(s) in 100% N<sub>2</sub> with lower temperature
- Pore volume decreases upon cycling and in more sintering conditions
- Densification observed upon cycling and in more sintering conditions
- Particle densification may be a significant mechanism for the deactivation of particles, in that large quantities of the pore volume required for CaCO<sub>3</sub> to grow from CaO are lost
- The amalgamation and migration of pores has previously been suggested to explain the loss of microporous volume upon cycling and the results here can be taken as evidence for this hypothesis

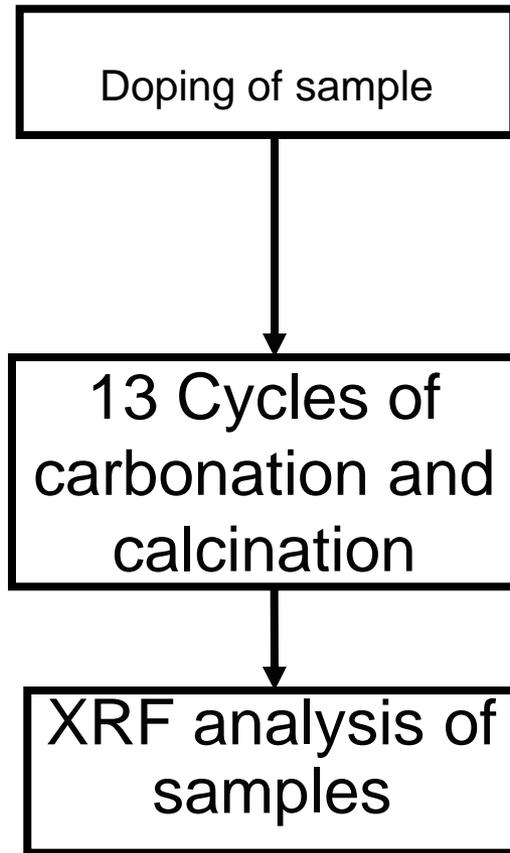
## Collaboration with INCAR

- Collaboration has been initiated between the Instituto Nacional del Carbon (INCAR) in Spain and Imperial College, London



- INCAR has a pilot plant facility investigating the calcium looping cycle
  - Dual circulating fluidised bed
- B Gonzalez compared two samples by repeatedly cycling them in a TGA:
  - Limestone taken from the pilot plant
  - The original limestone

## Collaboration with INCAR: Experimental Work

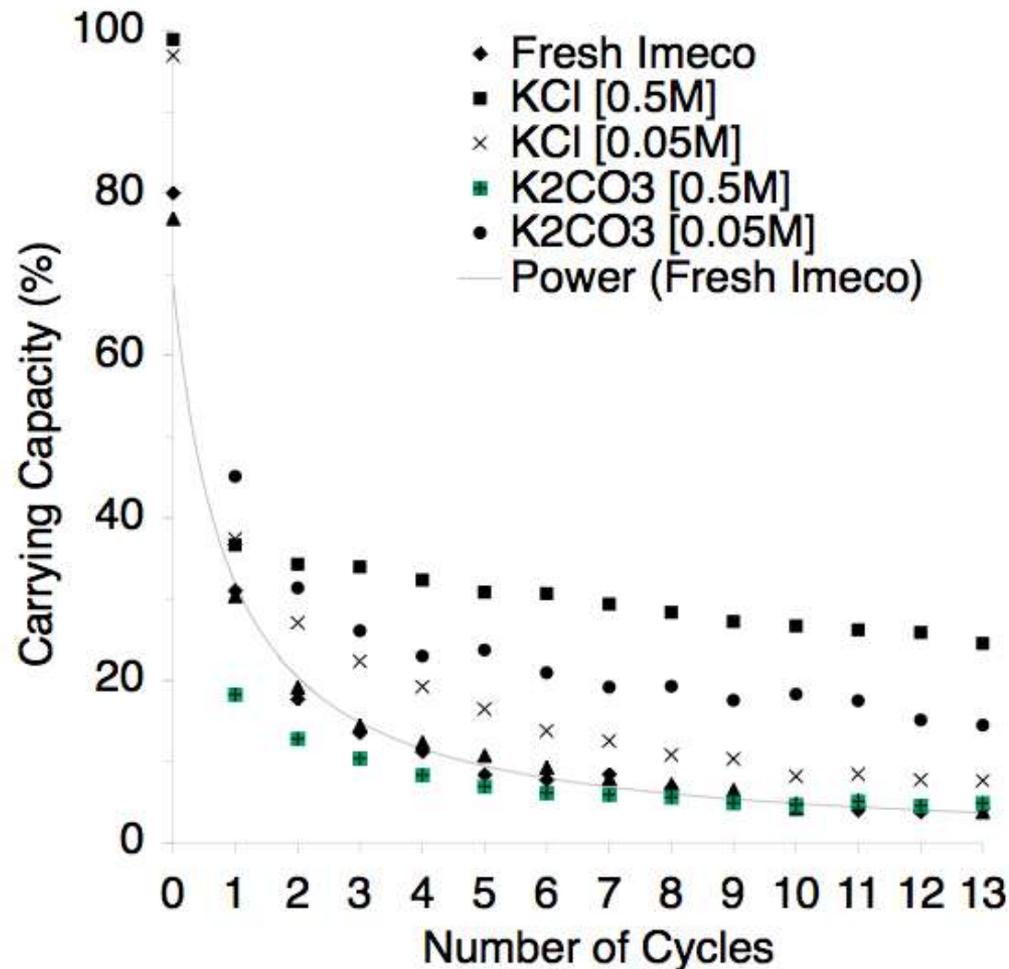


**Doping sample:** Created standard solutions of KCl and  $K_2CO_3$  at 0.05 M and 0.5 M. Left 20 g of Imeco limestone in 800 mL solution for 40 h. Decanted sample and put in oven overnight at 100 °C to dry slowly.

**Standard cycling experiments:** 15%  $CO_2$ , atmospheric pressure, 13 cycles of carbonation at 700 °C for 600 s and calcination at 900 °C for 600 s, 4.3 g Imeco limestone (500-710  $\mu m$ ) in 8 mL bed of sand (355-425  $\mu m$ ), flow rate  $\sim 8 U/U_{mf}$

**Variables investigated:** Extent of doping, effect of changing salt concentration and effect of different salts.

## Collaboration with INCAR: Preliminary results



- Results were unexpected
- Doping seemed to increase carrying capacity in some cases
- Imeco limestone used is very friable
- Could the improved carrying capacity be due to particle agglomeration?
- Potassium compounds have low melting points
  - KCl = 775 degC
  - K<sub>2</sub>CO<sub>3</sub> = 891 degC
- Agglomeration was so extreme in case of K<sub>2</sub>CO<sub>3</sub> that fluidisation was observed to stop.

## Useful Engagement with the USA

Mainly concerned with involvement in large-scale demonstrations.

Currently, there are plans for or more Ca looping demonstration projects in the USA.

It would make sense for these projects to be aligned well with EU / Can demonstration projects and UK fundamental research.

## Thank you for listening...

Funded by the Engineering and Physical Sciences Research Council (EPSRC), UK, The European Union, the Royal Society / Wolfson fund, and a number of companies.

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- V. Manovic, J.-P. Charland, J. Blamey, P.S. Fennell, D.Y. Lu, and E.J. Anthony. *Influence of calcination conditions on carrying capacity of CaO-based sorbent in CO<sub>2</sub> looping cycles*. Fuel, 2009. 88(10): p. 1893-1900.
- Y. Wu, J. Blamey, E.J. Anthony and P.S. Fennell. *Morphological Changes of Limestone Sorbent Particles during Carbonation/Calcination Looping Cycles in TGA and Reactivation with Steam*. Accepted by Energy and Fuels, 2010.
- J. Blamey, N.P.M. Paterson, D.R. Dugwell, P. Stevenson, P.S. Fennell. *Reactivation of a CaO-Based Sorbent for CO<sub>2</sub>*. Submitted to the Combustion Symposium, 2010.