

# Development and testing of sorbents for high temperature solid-looping CO<sub>2</sub> capture

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# The Novel C-SHIFT Process for Efficient Low-Carbon H<sub>2</sub> and Power Production

**Pressurised Kinetic Measurements of CO<sub>2</sub> Capture by K-Promoted Hydrotalcites in a High Steam Atmosphere**

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FERF Environment Interest  
Group Inaugural Seminar  
University of Sheffield, UK  
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## Presentation Overview

- Introduction to C-SHIFT and ENDEX technology
- Hydrotalcite-derived CO<sub>2</sub> sorbents- What are they and why?
- Sorbent testing using a pressurised fluidised (spouted) bed reactor
- Results
- Conclusions



# The Carbonated-Shift (C-Shift) Process

What is it?

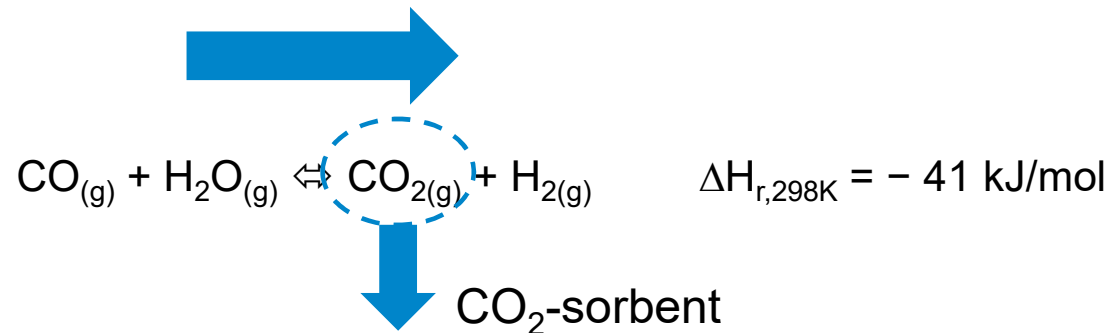


## The Carbonated-Shift (C-Shift) Process

**C-Shift** combines the concepts of **sorbent enhanced water-gas shift (SEWGS)** with **ENDEX sorbent regeneration technology**.

### SEWGS

**Water-gas shift:**

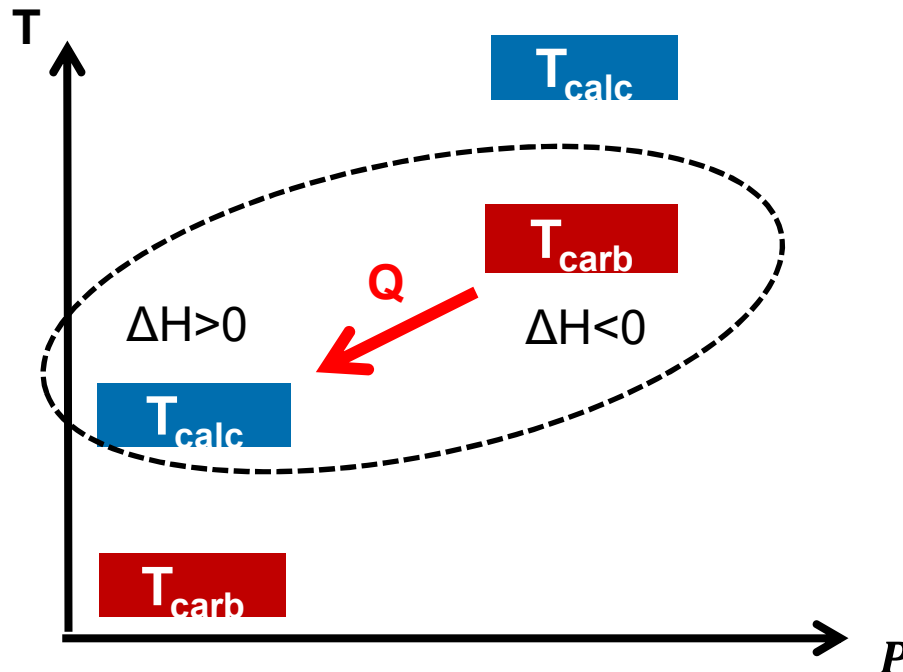


**SEWGS removes  $\text{CO}_2$  from system shifting equilibrium in favour of  $\text{H}_2$  production**

# The Carbonated-Shift (C-Shift) Process

**C-Shift** combines the concepts of **sorbent enhanced water-gas shift (SEWGS)** with **ENDEX sorbent regeneration technology**.

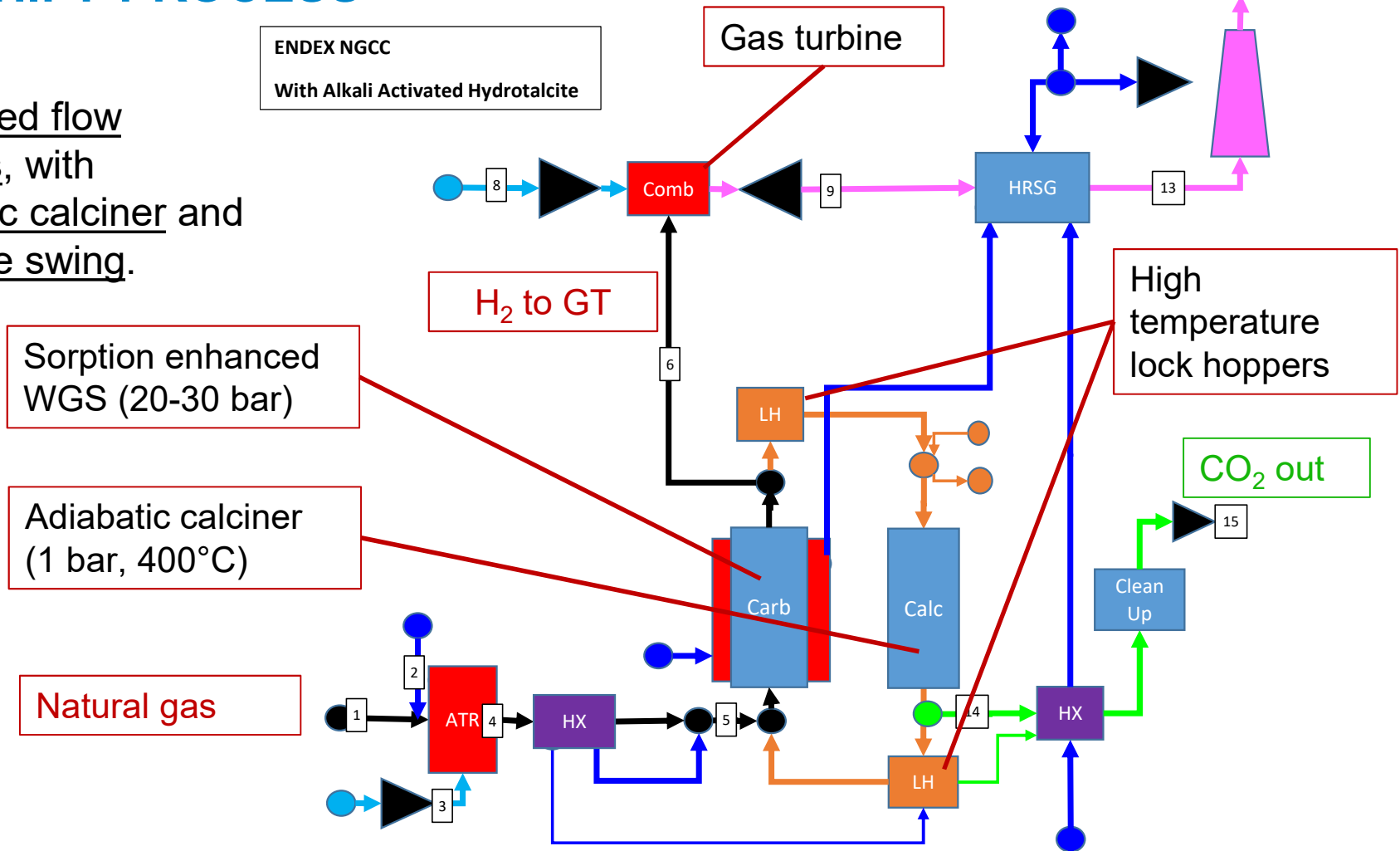
**ENDEX**  
(**END**othermic-**EX**othermic)



- **Heat released** during exothermic **carbonation** is exploited to **provide the heat necessary** to drive the endothermic **calcination** reaction
- Harness the effect of  $CO_2$  partial pressure on equilibrium constants
- Effect **carbonation** at a **higher temperature** than calcination at atmospheric pressure
- **Calcination** achieved by **P-swing**
- Thermally integrated carbonator and calciner

## C-SHIFT PROCESS

Entrained flow  
reactors, with  
adiabatic calciner and  
pressure swing.



# **C-Shift Sorbent Selection Criteria**

**&**

## **Introduction to Benchmark C-Shift Sorbent Hydrotalcite-derived CO<sub>2</sub> sorbents**





## C-SHIFT Sorbent Selection Criteria

- $\text{CaCO}_3/\text{CaO}$  –most commonly investigated sorbent for SEWGS and ENDEX processes

### However

- Very high operating temperatures (800-1000 °C) necessary for ENDEX operation
  - Engineering challenges
  - Enhanced sorbent degradation issues
  - Safety Concerns

### Therefore

- An **alternative sorbent** capable at operating within a more **moderate temperature range** is desirable.

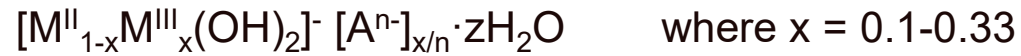


## C-SHIFT Sorbent Selection Criteria

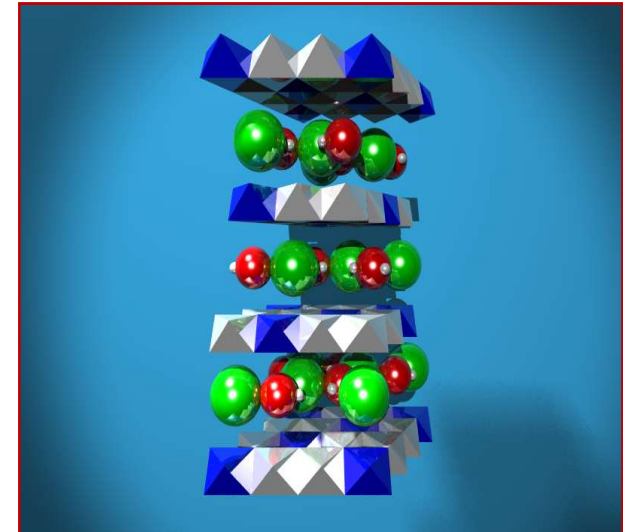
- Proven affinity with CO<sub>2</sub> at relevant process conditions (**300-800 °C; 1-40 bar<sub>a</sub>**).
  - CO<sub>2</sub> carrying capacity of 5 – 15 wt% (**1.1-3.4 mmol CO<sub>2</sub>/g sorbent**)
  - Fast kinetics for WGS & CO<sub>2</sub> capture at relevant process conditions  
*i.e.* capable of providing > 90 % CO<sub>2</sub> capture in a single pass reactor no larger than 12 m in height (***i.e.* residence times of < 60 s**).
  - Precursors – Low cost, widely available and currently being manufactured at an industrial scale.
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## Benchmark Sorbent- $K_2CO_3$ -promoted Hydrotalcites (K-HTCs)

- Layered double hydroxide (LDH) with general formula:



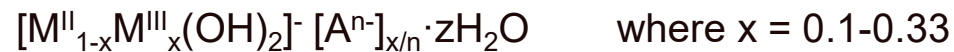
- $Mg^{2+}/Al^{3+}$ -HTCs are typically investigated for high T  $CO_2$  sorption



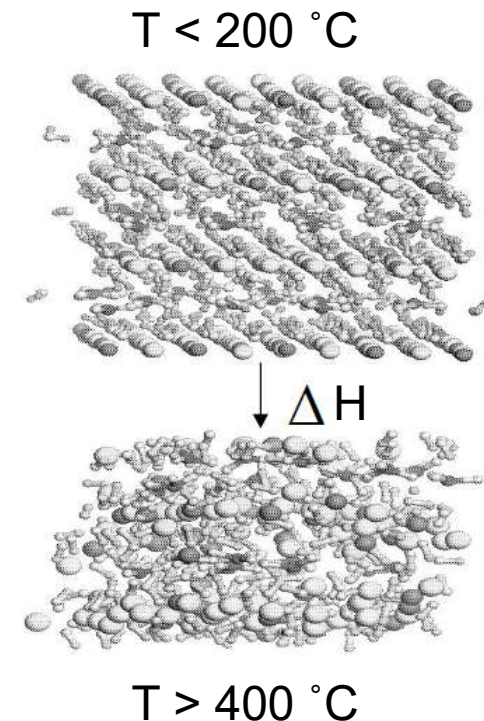
Structure of layered double hydroxide

## Benchmark Sorbent- $K_2CO_3$ -promoted Hydrotalcites (K-HTCs)

- Layered double hydroxide (LDH) with general formula:



- $Mg^{2+}/Al^{3+}$ -HTCs are typically investigated for high T  $CO_2$  sorption (300-500 °C)
- Calcination yields highly disorganised amorphous mixed metal oxide – active phase for  $CO_2$  sorption.
- Carbonation mechanisms activated by impregnation with  $K_2CO_3$  and presence of high pressure steam<sup>1</sup>



MD Simulations from  
Tsotsis et al. *J. Chem. Phys.* **2005**, 122, 214713

- $CO_2$  sorption capacities up to **15.1 mmol g<sup>-1</sup>** \* have been reported for HTC 11wt%  $K_2CO_3$  loading Mg/Al ratio = 2.9

\* Autoclave, 350 °C, 40 bar<sub>a</sub>, P<sub>CO<sub>2</sub></sub> = 20 bar<sub>a</sub>, P<sub>H<sub>2</sub>O</sub> = 20 bar<sub>a</sub>, t<sub>carb</sub> = 2 hrs

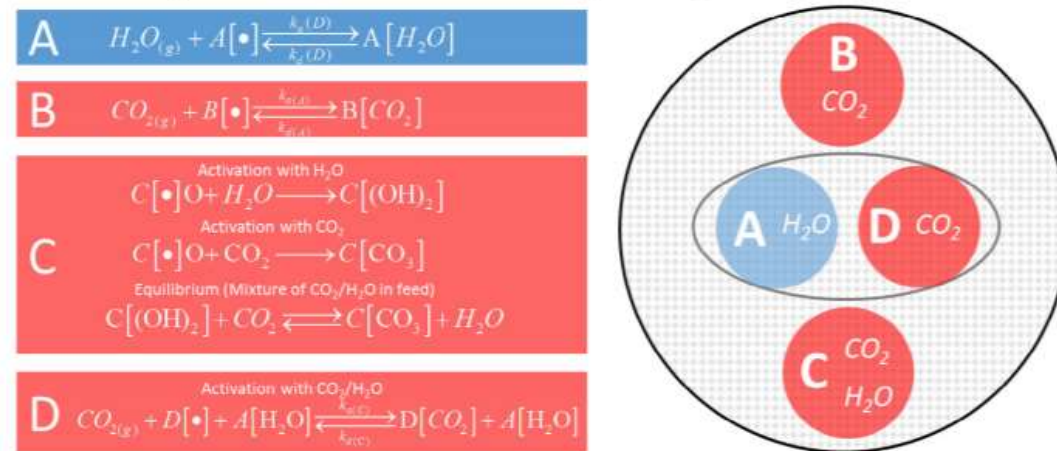
\* Walspurger, S. et al. *Chemistry-A European Journal* **2010** 16(42) 12694-12700

## Benchmark Sorbent- $K_2CO_3$ -promoted Hydrotalcites (K-HTCs)

### Proposed Carbonation Mechanisms

- (i) Fast but weak interaction on the surface and in the interlayers- enhanced by  $K_2CO_3$  forming weak  $K-CO_3-Al$  type phase (**steam enhanced**)

Recently Coenen et al. provided evidence for the existence of **3 sites** for  **$CO_2$  adsorption**

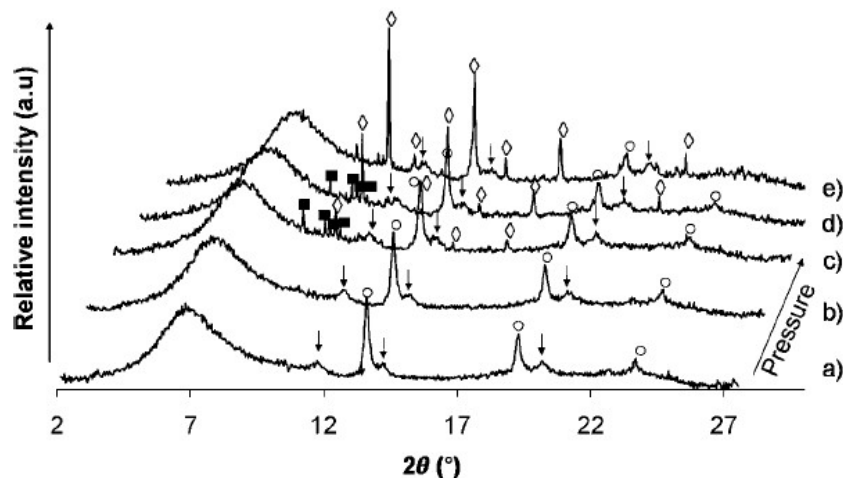


Coenen, K. et al. Chemical Engineering Journal **2017** 314 554–569.

## Benchmark Sorbent- $K_2CO_3$ -promoted Hydrotalcites (K-HTCs)

### Proposed Carbonation Mechanisms

- (i) Fast but weak interaction on the surface and in the interlayers- enhanced by  $K_2CO_3$  forming weak  $K-CO_3-Al$  type phase (**steam enhanced**)
  - (ii) Fast "ish" surface  $MgCO_3$  formation
  - (iii) Slow bulk  $MgCO_3$  formation
- ( high pressure steam and  $K_2CO_3$  activated)



◇  $MgCO_3$  only starts to form at elevated pressure in the presence of steam

## Benchmark Sorbent- $K_2CO_3$ -promoted Hydrotalcites (K-HTCs)

### **K22-MG70 (250-355 $\mu\text{m}$ )**

- **HTC produced by Sasol comprised of 70 wt% MgO / 30 wt%  $Al_2O_3$**
- **promoted with 22 wt%  $K_2CO_3$**



# Sorbent Testing at Imperial College:

Determination of Carbonation Kinetics and Capacities at C-Shift  
Relevant Conditions and Time-Scales (i.e. < 60 s)

$T = 300\text{-}500\text{ }^{\circ}\text{C}$

$P_{\text{CO}_2} = 0.5\text{-}5\text{ bar (NG-CSHIFT)}$

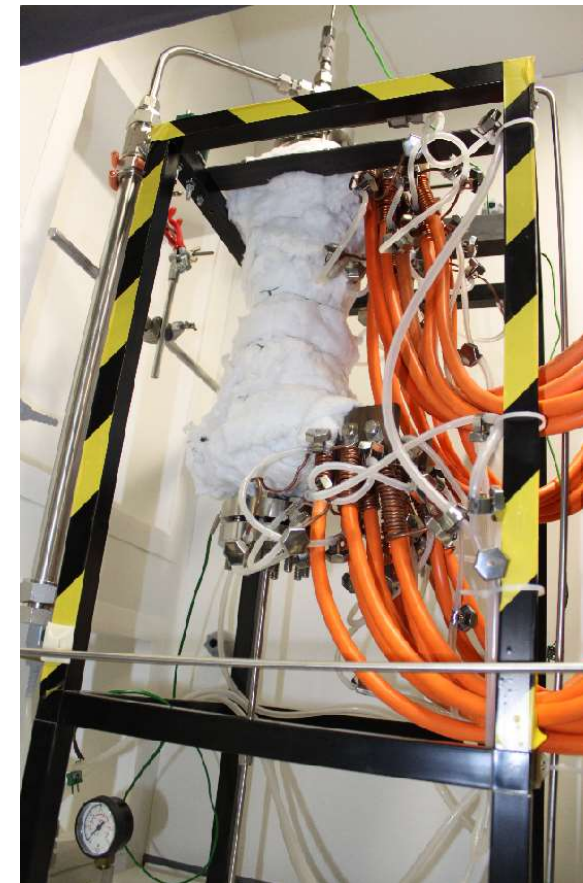
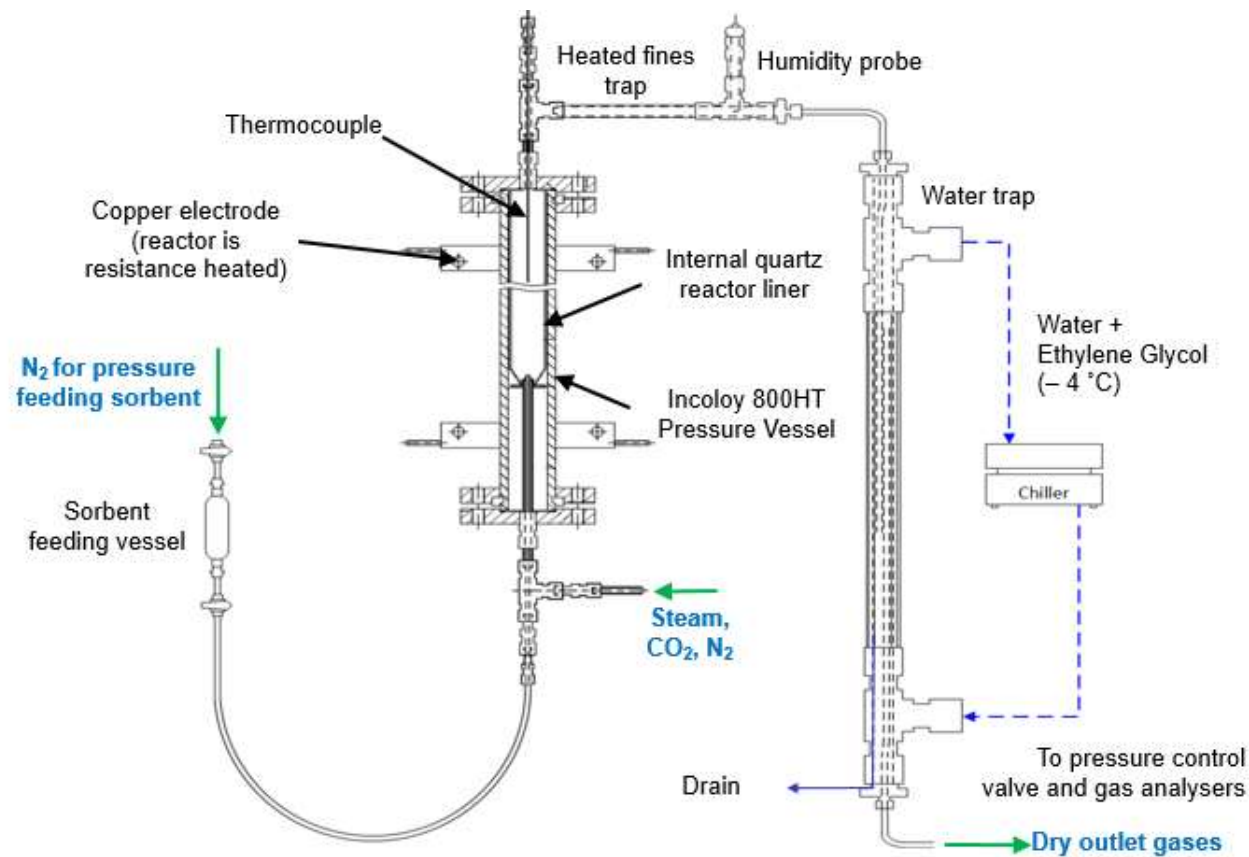
$P_{\text{H}_2\text{O}} = 0\text{-}4\text{ bar}$

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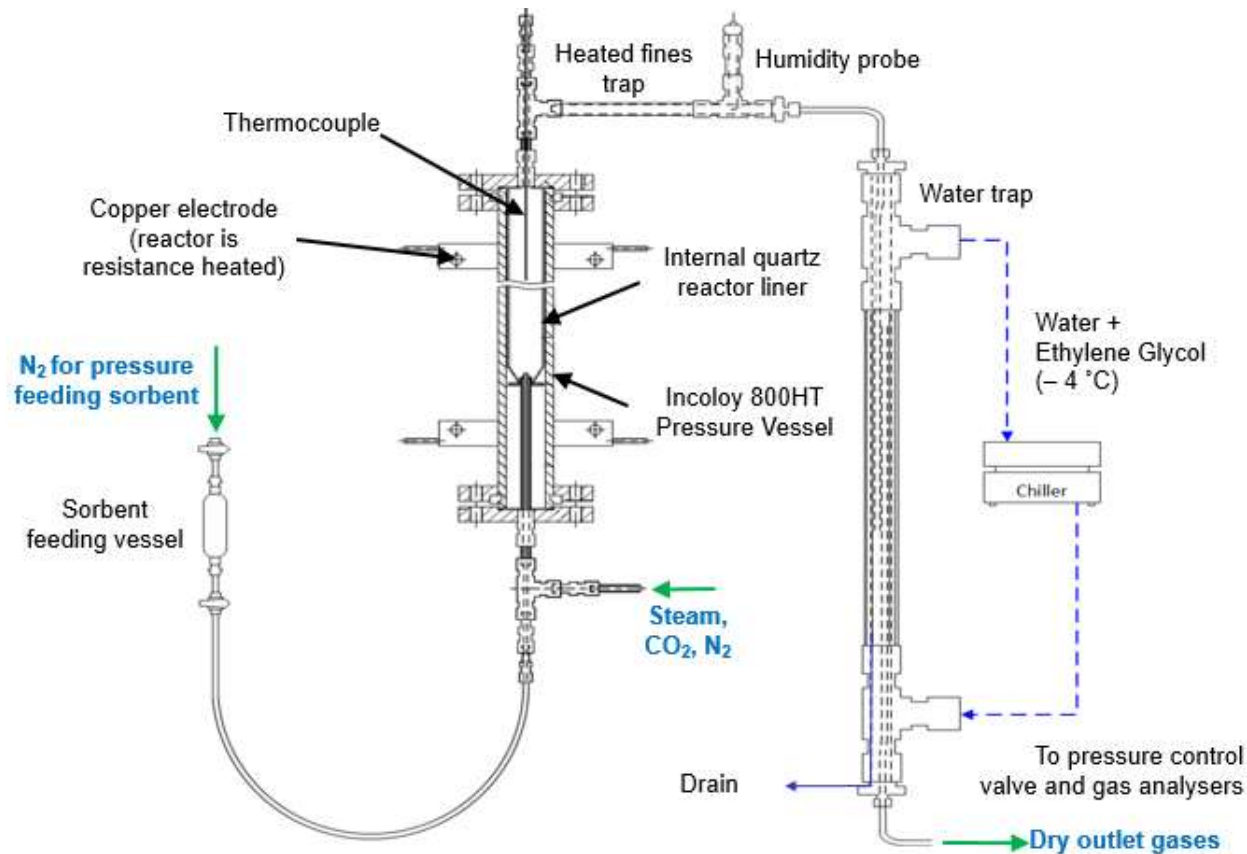
## Sorbent Evaluation at C-Shift Relevant Conditions

### Pressurised fluidized bed (spouted bed) reactor



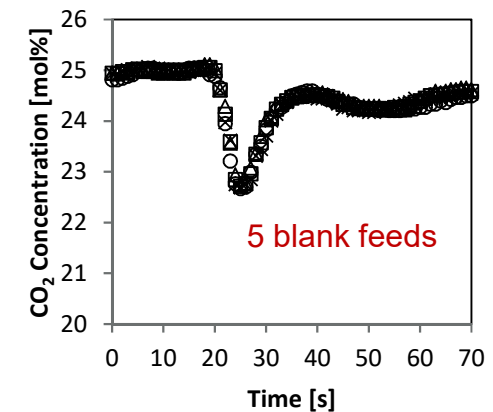
# Sorbent Evaluation at C-Shift Relevant Conditions

## Pressurised fluidized bed (spouted bed) reactor



## Experimental Protocol

1. Experimental conditions are established and stabilised
2. Blank Feed

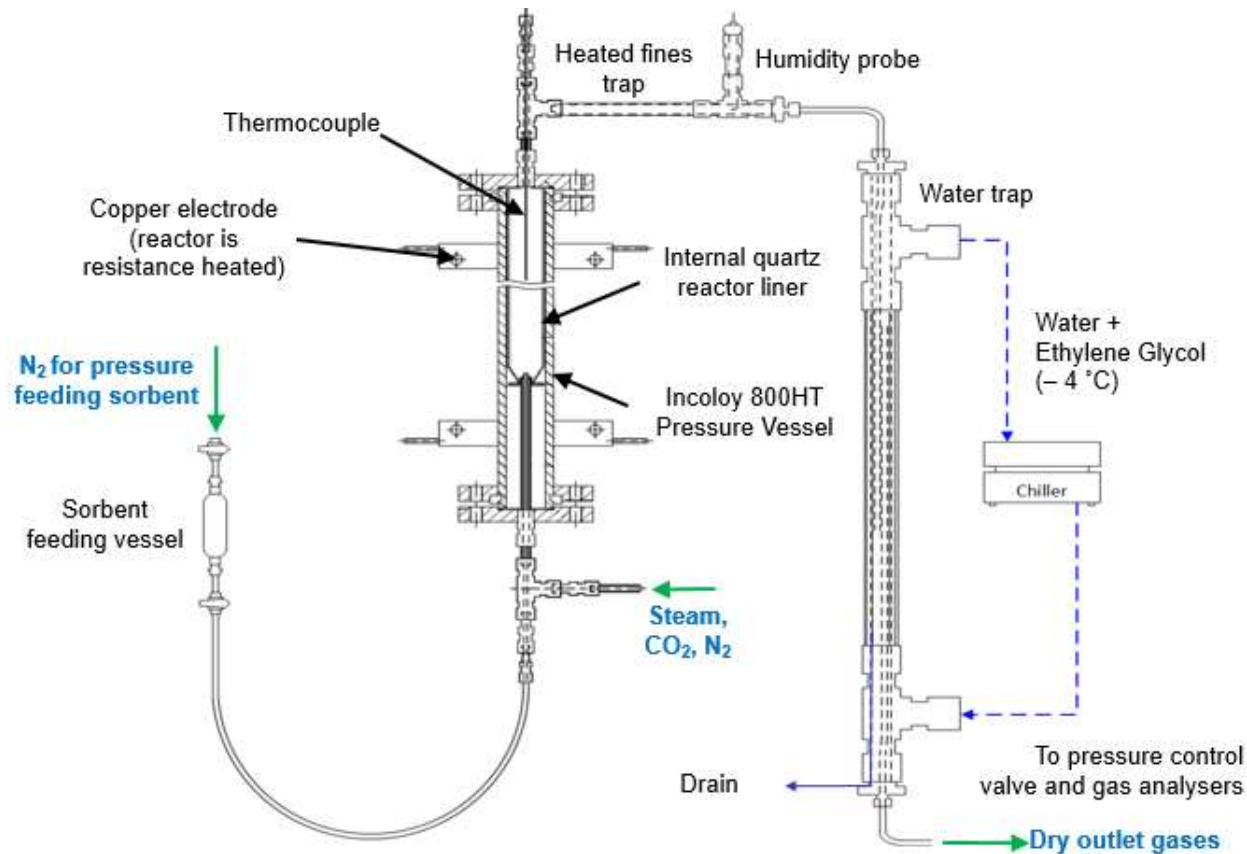


### Experimental Conditions:

T= 400 °C, P= 10 bar<sub>a</sub>, [CO<sub>2</sub>]= 20 mol%, [H<sub>2</sub>O] = 40 mol%,

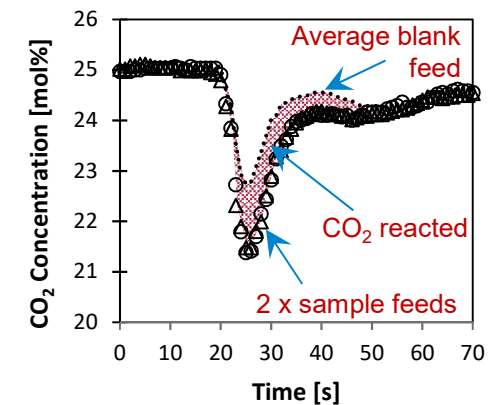
# Sorbent Evaluation at C-Shift Relevant Conditions

## Pressurised fluidized bed (spouted bed) reactor



## Experimental Protocol

1. Experimental conditions are established and stabilised
2. Blank Feed
3. Sorbent fed into reactor

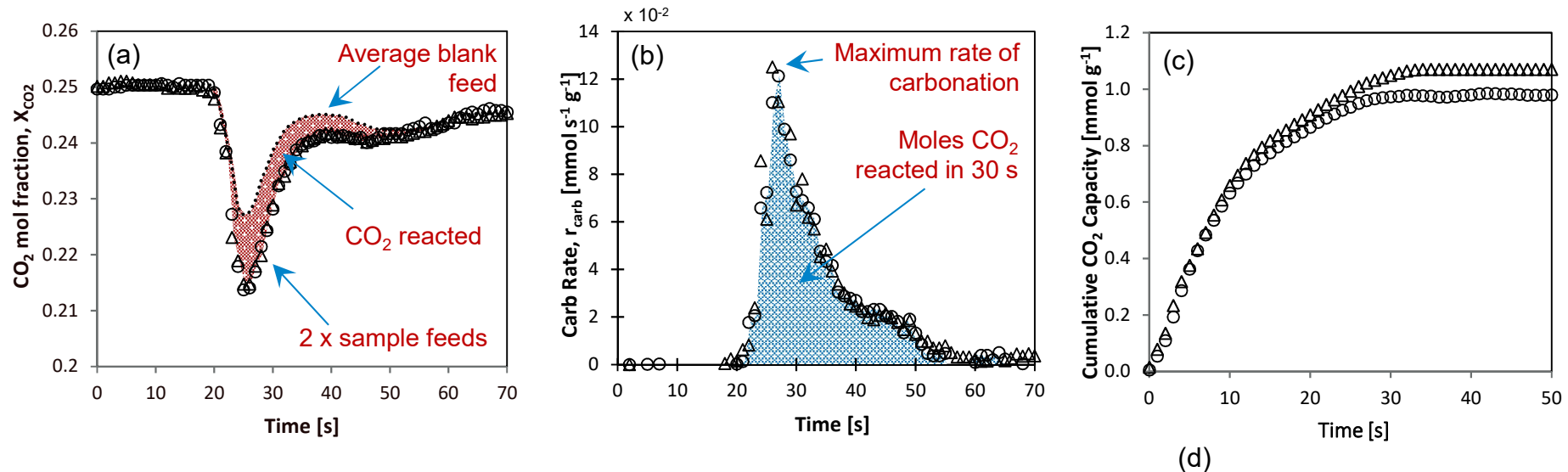


### Experimental Conditions:

$T = 400\text{ }^{\circ}\text{C}$ ,  $P = 10\text{ bar}_a$ ,  $[\text{CO}_2] = 20\text{ mol\%}$ ,  $[\text{H}_2\text{O}] = 40\text{ mol\%}$ ,

## Determination the rate and extent of carbonation for fast initial carbonation reaction (0-30 s)

**Carbonation Conditions:** T= 400 °C, P= 10 bar<sub>a</sub>, [CO<sub>2</sub>]= 2 bar<sub>a</sub>, [H<sub>2</sub>O] = 4 bar<sub>a</sub> Sorbent = K22-MG70-M-PLT (2 g, 250-355 µm)



- The rate of carbonation,  $r_{carb}$  (in mmol s<sup>-1</sup> g<sup>-1</sup>) was calculated using the following equation:

$$r_{carb} = \frac{Q_{in}(X_{CO_2,in} - X_{CO_2,out})}{(1 - X_{CO_2,out})}$$

- The cumulative uptake capacity (c) for the initial fast reaction is readily obtained by integrating the rate profile with respect to time (blue area in (b)).

# Sorbent Testing at Imperial College:

## Results

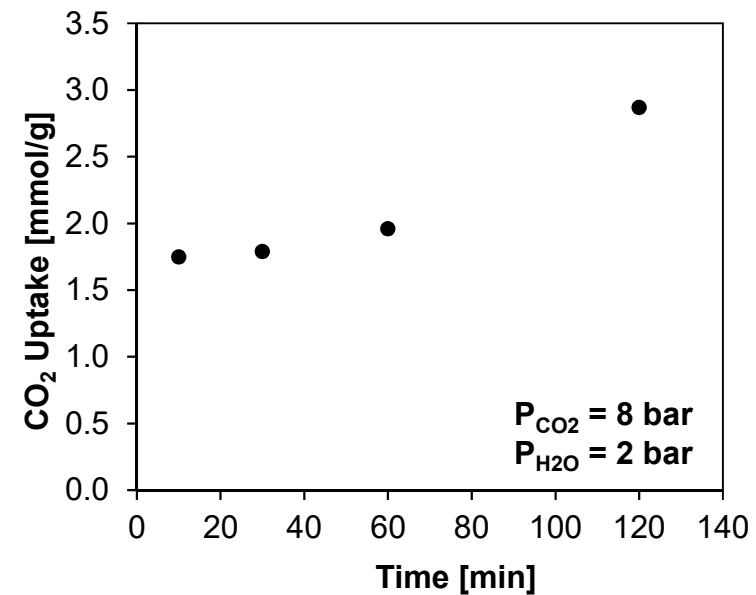
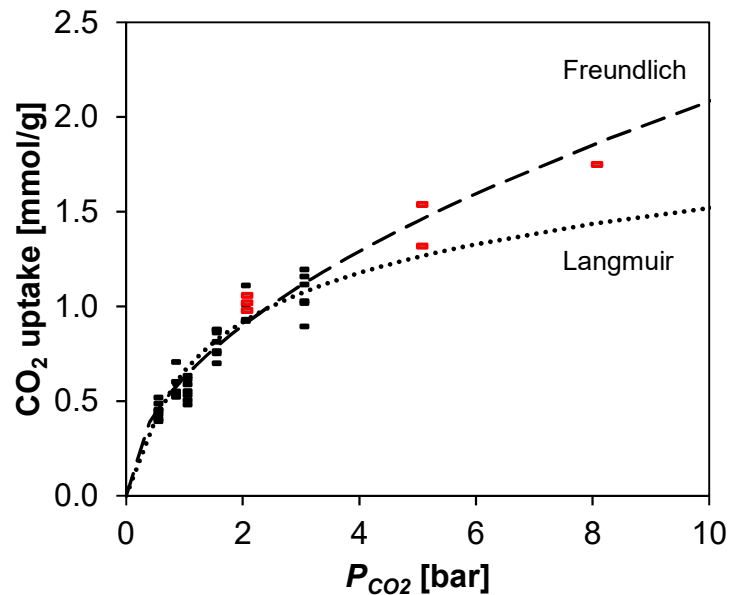
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## CO<sub>2</sub> Sorption Capacity Increased with Increasing $P_{CO_2}$

### Carbonation Conditions:

$T = 400\text{ }^{\circ}\text{C}$ ,  $P = 3\text{--}10\text{ bar}_a$ ,  $[CO_2] = 0\text{--}3\text{ bar}$  (& **2-8 bar**),  $[H_2O] = 4\text{ bar}$ ,  $t_{carb} = 30\text{ s}$  (& **600 s**)

Sorbent = K22-MG70-M-PLT (1.0 / 2.0 g, 250-355  $\mu\text{m}$ )



Isotherm Projections of working capacity at NG-CSHIFT conditions ( $P_{CO_2, carb} = 5.5\text{ bar}$ ,  $P_{CO_2, cal} = 0.5\text{ bar}$ ) **0.9-1.3 mmol/g**

**Sorbent more suitable for coal-IGCC-CSHIFT** where  $P_{CO_2} \geq 10\text{ bar}$  (**1.1-1.6 mmol/g** (10 bar<sub>CO<sub>2</sub></sub>), **1.4-3.0 mmol/g** (20 bar<sub>CO<sub>2</sub></sub>) and **1.5-3.7 mmol/g** (30 bar<sub>CO<sub>2</sub></sub>))

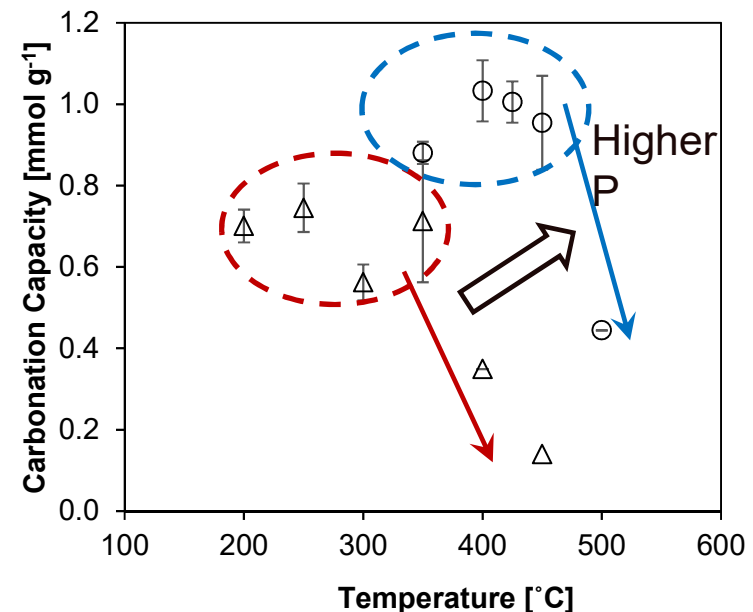
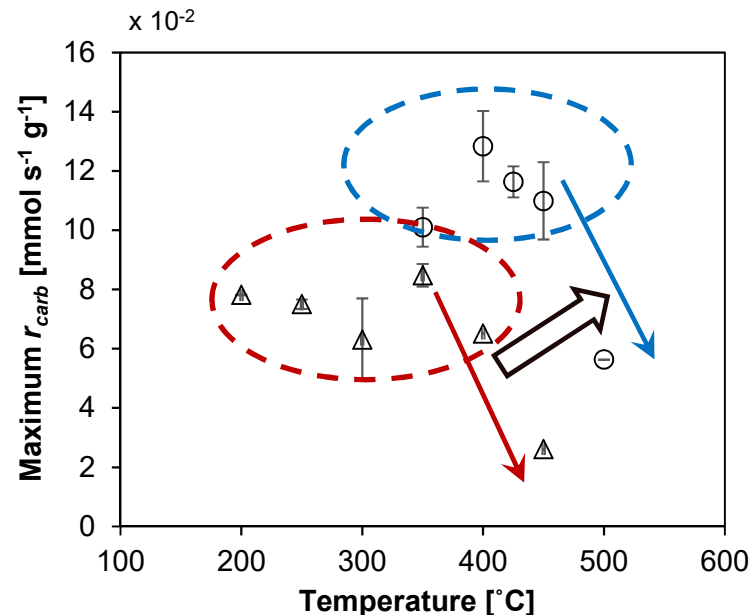


## Increasing the $P_{CO_2}$ increases the temperature at which sorbent carbonation can be achieved

### Carbonation Conditions:

△ T= 200-400 °C,  $P_{Tot}$  = 5 bar<sub>a</sub>,  $[CO_2]$  = **1 bar**, S/C = 1,  $t_{carb}$  = 30 s Sorbent = K22-MG70-M-PLT (1.0 g, 250-355 µm)

○ T= 350-500 °C,  $P_{Tot}$  = 10 bar<sub>a</sub>,  $[CO_2]$  = **2 bar**, S/C = 1,  $t_{carb}$  = 30 s Sorbent = K22-MG70-M-PLT (2.0 g, 250-355 µm)



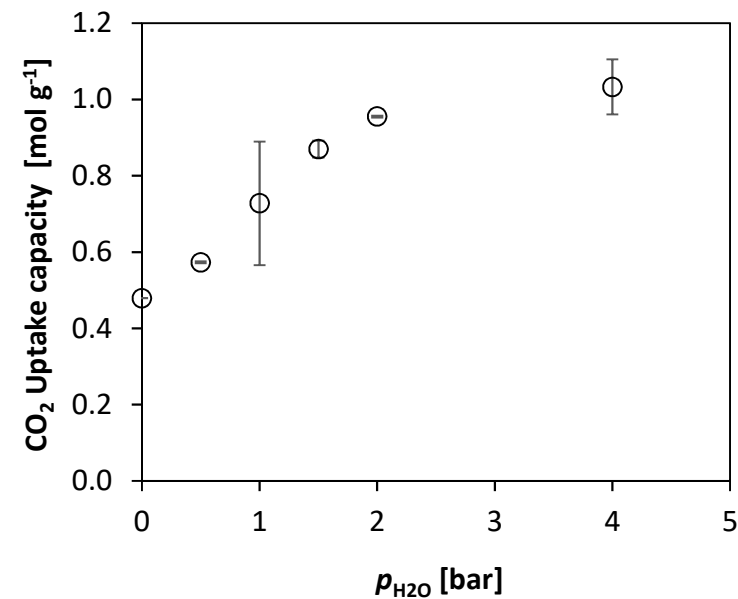
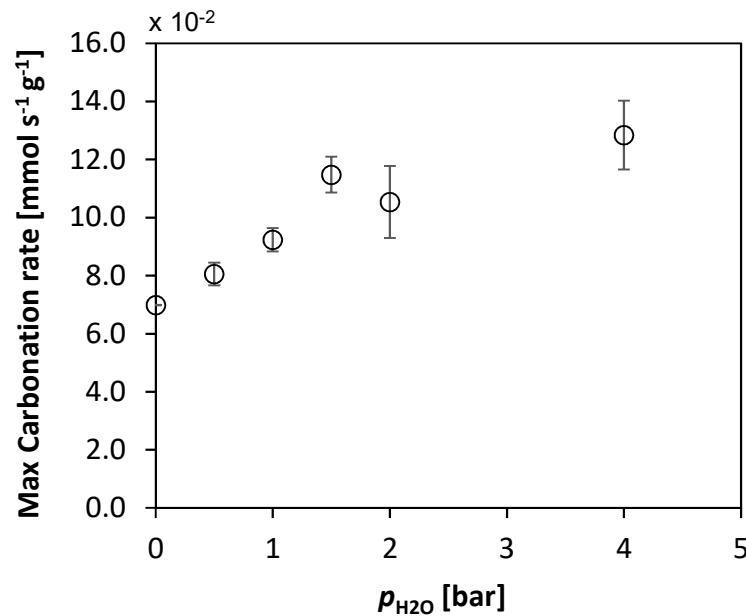
Lower T – Carbonation rate and capacity relatively stable

**Rate** and **capacity** starts to **decay** at ~350-400 °C at 1 bar<sub>CO2</sub> → shifted to 450-500 °C at 2 bar<sub>CO2</sub>

## Presence of steam up to S/C ratio of 1 causes significant improvement in the carbonation rate and capacity

### Carbonation Conditions:

$T = 400\text{ }^{\circ}\text{C}$ ,  $P = 10\text{ bar}_a$ ,  $p_{\text{CO}_2} = 2\text{ bar}$ ,  $p_{\text{H}_2\text{O}} = 0\text{--}4\text{ bar}$ ,  $t_{\text{carb}} = 30\text{ s}$  Sorbent = K22-MG70-M-PLT (2.0 g, 250-355  $\mu\text{m}$ )



Increasing steam concentration from 0-2 bar (S/C =1) Carbonation capacity increased **0.41  $\rightarrow$  1.01  $\text{mmol g}^{-1}$**

Influence of steam transitions to a **zero order relationship between 2 bar and 4 bar (S/C 1  $\rightarrow$  2)**



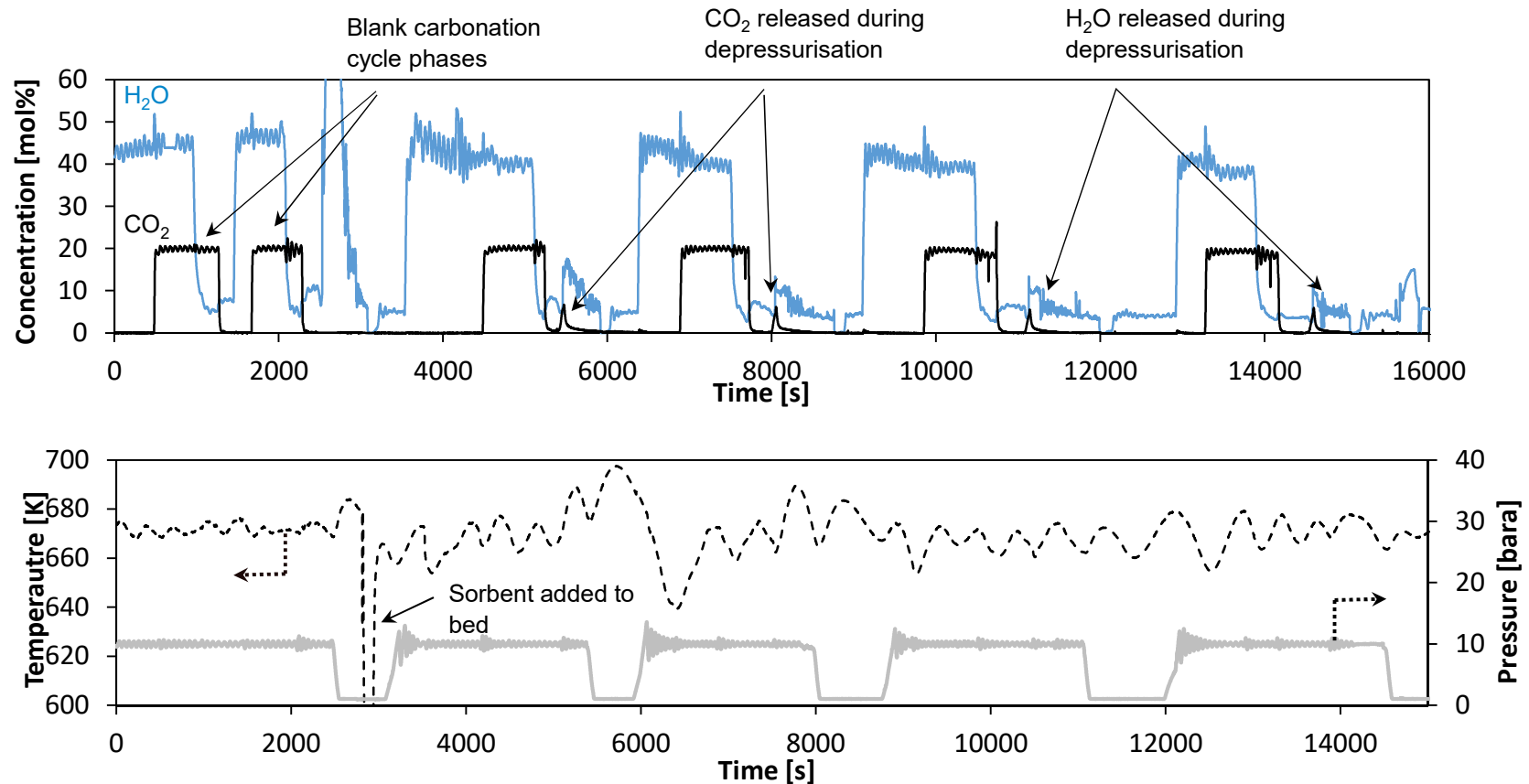
## Stable CO<sub>2</sub> Sorption Capacities of ~ 1 mmol/g over 10 cycles



**Carbonation Conditions:** T= 400 °C, P= **10 bar<sub>a</sub>**, [CO<sub>2</sub>] = 20 mol%, [**H<sub>2</sub>O**] = **40 mol%**, t<sub>carb</sub> = 600 s

**Calcination Conditions:** T= 400 °C, P= **10 → 1 bar<sub>a</sub>**, [CO<sub>2</sub>] = 0 mol%, [**H<sub>2</sub>O**] = **0 mol%**, t<sub>cal</sub> = ~600 s

**Sorbent:** K22-MG70-M-PLT (20 g, 250-355 μm)



## Conclusions

- Increasing Carbonation Partial Pressure → Increase in Carbonation rate and initial fast uptake capacity  
**Maximum measured capacity =  $1.03 \text{ mmol g}^{-1}$**
- Projected working capacity-  **$0.9\text{-}1.1 \text{ mmol/g}$**  at NG-CSHIFT conditions ( $P_{\text{CO}_2, \text{carb}} = 5.5 \text{ bar}$ ,  $P_{\text{CO}_2, \text{cal}} = 0.5 \text{ bar}$ )  
 $P_{\text{CO}_2} \geq 10 \text{ bar}$  ( **$1.1\text{-}1.6 \text{ mmol/g}$**  ( $10 \text{ bar}_{\text{CO}_2}$ ),  **$1.4\text{-}3.0 \text{ mmol/g}$**  ( $20 \text{ bar}_{\text{CO}_2}$ ) and  **$1.5\text{-}3.7 \text{ mmol/g}$**  ( $30 \text{ bar}_{\text{CO}_2}$ ))
- Increasing steam concentration from 0-2 bar (S/C =1) → Significant improvement in rate and initial fast uptake capacity  
**Maximum measured capacity increased  $0.41 \rightarrow 1.01 \text{ mmol/g}$  (~ 150% increase)**
- Limited additional improvement in  $\text{CO}_2$  sorption kinetics/capacity for S/C > 1
- Preliminary screening to determine suitability of AA-Mag based sorbents for NG-CSHIFT applications has commenced

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Thank you for your attention



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**ASCENT Project webpage.** Available from: <http://ascentproject.eu/>