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# Pressurised Carbonation Experiments in the Presence of Steam in a Spouted Bed Reactor

By

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# Outline

- Background
- Experimental Setup and Procedure
- Results of Carbonation with Steam
- Summary

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# Background

Calcium Looping:

- Cycling CaO-based sorbents between two reactors (carbonator and calciner) to capture $CO_2$
- Experiments presented are focused on the carbonation process with the injection of steam

Effect of adding steam to the carbonation reaction from Literature:[1,2,3]

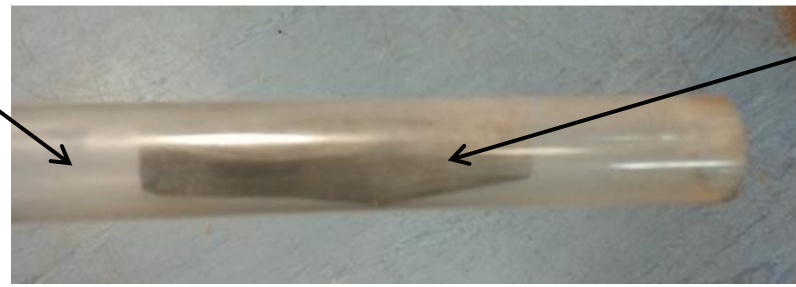
- Generally carried out in a TGA
- Mixed observations so no conclusive results


*1. Arias, B., Grasa, G., Abanades, J.C., Manovic, V., and Anthony, E.J., The Effect of Steam on the Fast Carbonation Reaction Rates of CaO. Industrial & Engineering Chemistry Research, 2012.* ***51(5)****: p. 2478-2482.*
*2. Donat, F., Florin, N.H., Anthony, E.J., and Fennell, P.S., Influence of High-Temperature Steam on the Reactivity of CaO Sorbent for* $CO_2$ *Capture. Environmental Science & Technology, 2012.* ***46(2)****: p. 1262-1269.*
*3. Manovic, V., and Anthony, E.J., Carbonation of CaO-BAsed Sorbents Enhanced by Steam Addition. Industrial & Engineering Chemistry Research, 2010.* ***49(19)****: p. 9105-9110.*

# Sorbent Preparation (Calcining Longcliffe Limestone)

Quartz Liner

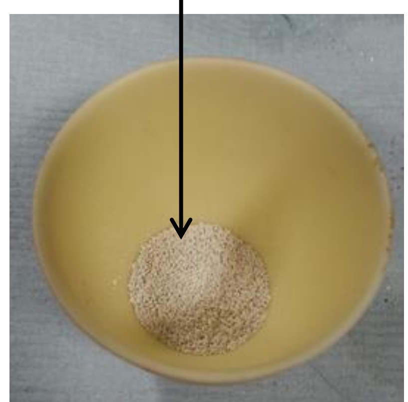
Raw Sample in wire mesh

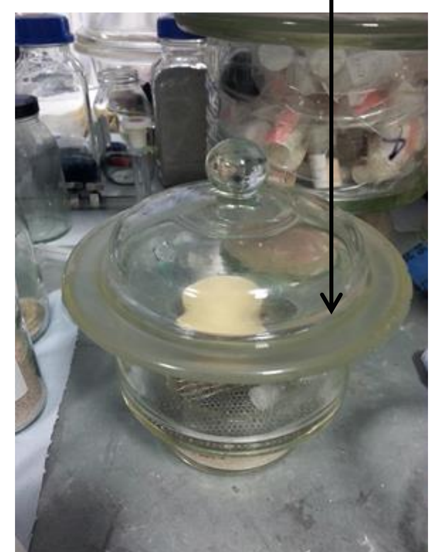


Horizontal Furnace

Cooled down in Desiccator

Calcined Sample





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# Sample (CaO) Properties

| Measurement | Average | Standard Deviation |
|---|---|---|
| BET Surface Area ($m^2/g$) | 19.40 | 3.28 |
| Envelope Density ($g/cm^3$) | 1.57 | 0.05 |
| Skeletal Density ($g/cm^3$) | 3.15 | 0.10 |
| Porosity <10 µm | 0.50 | 0.01 |

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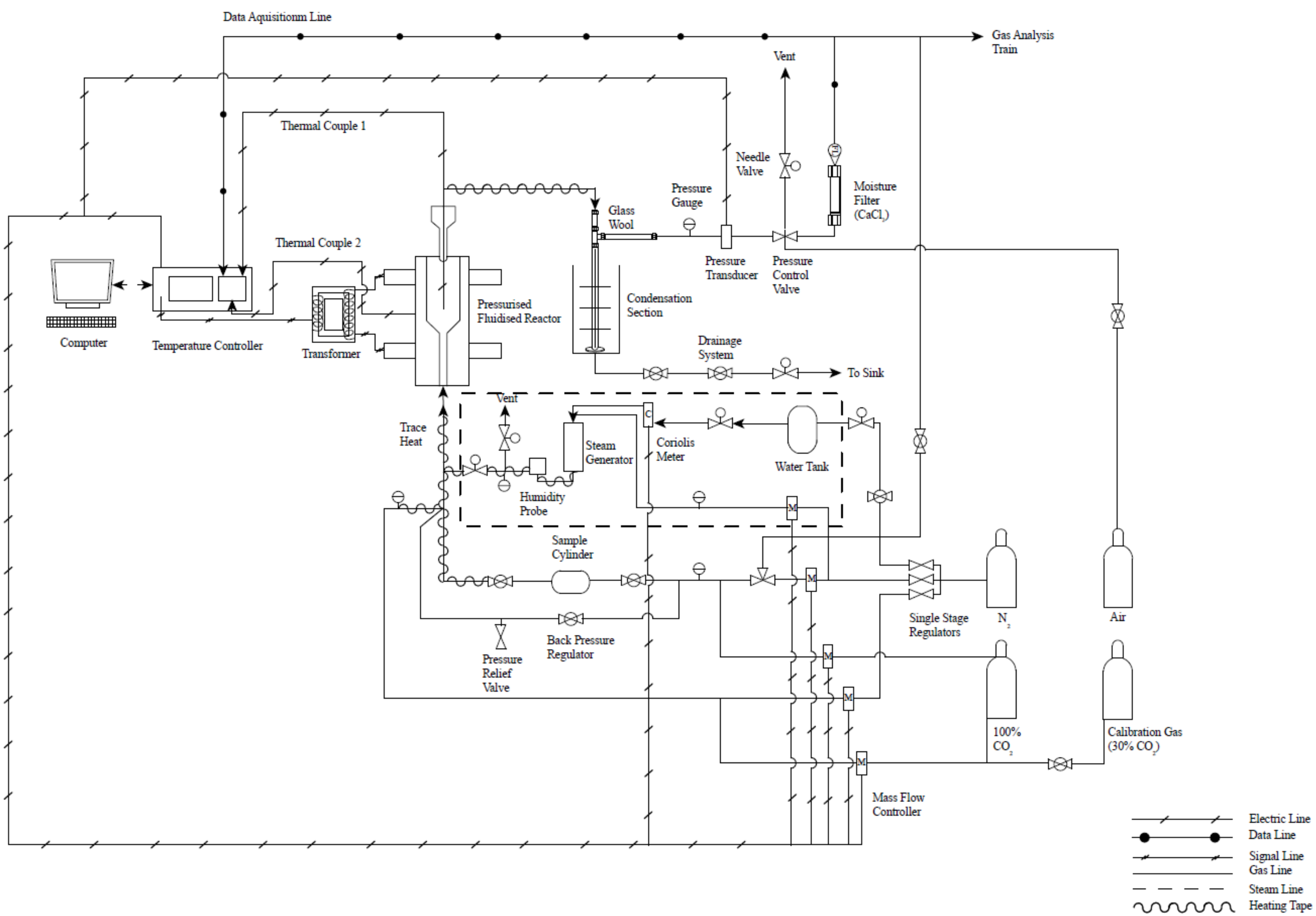
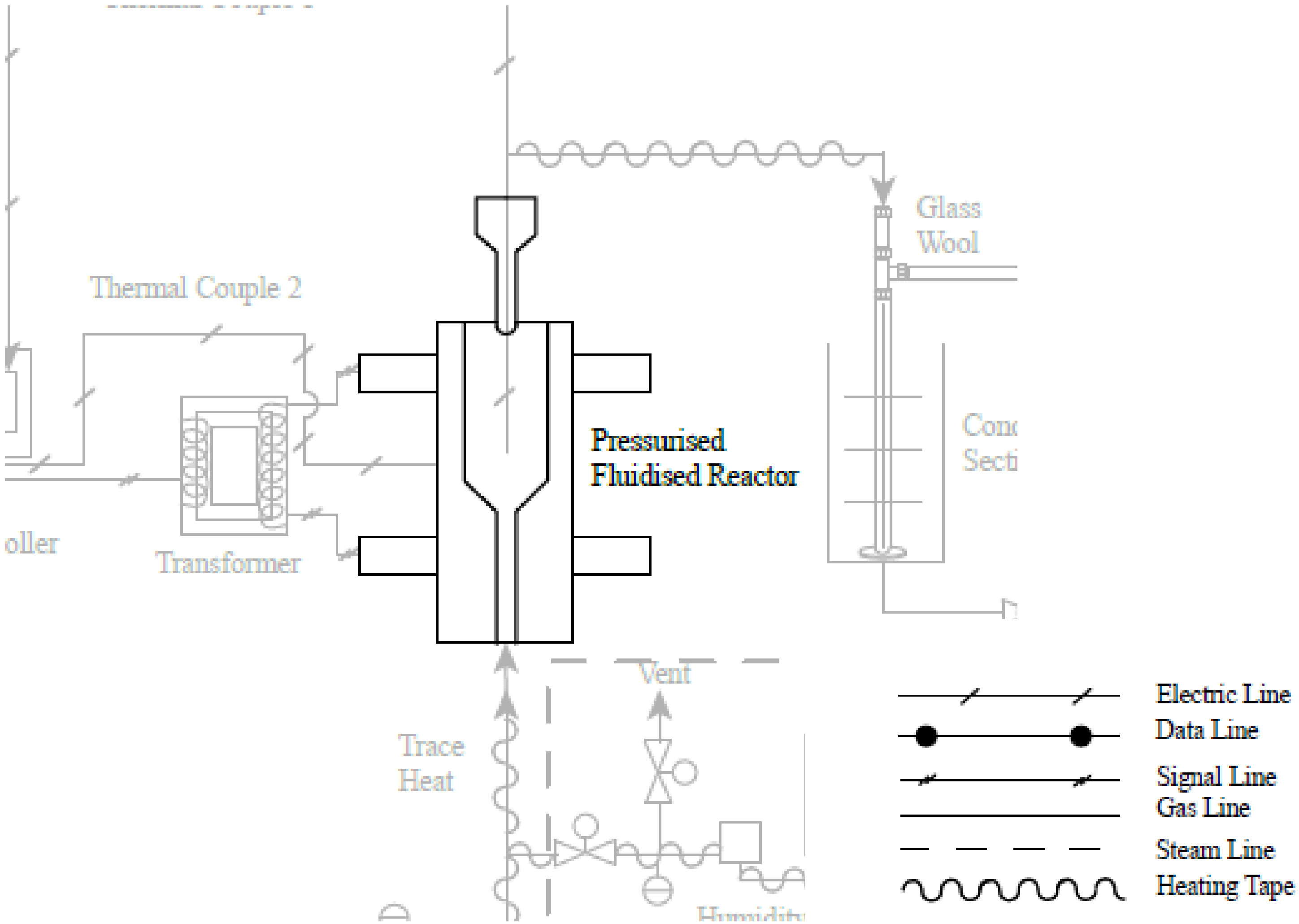
# Schematic of Rig



# Schematic of Rig: Reactor



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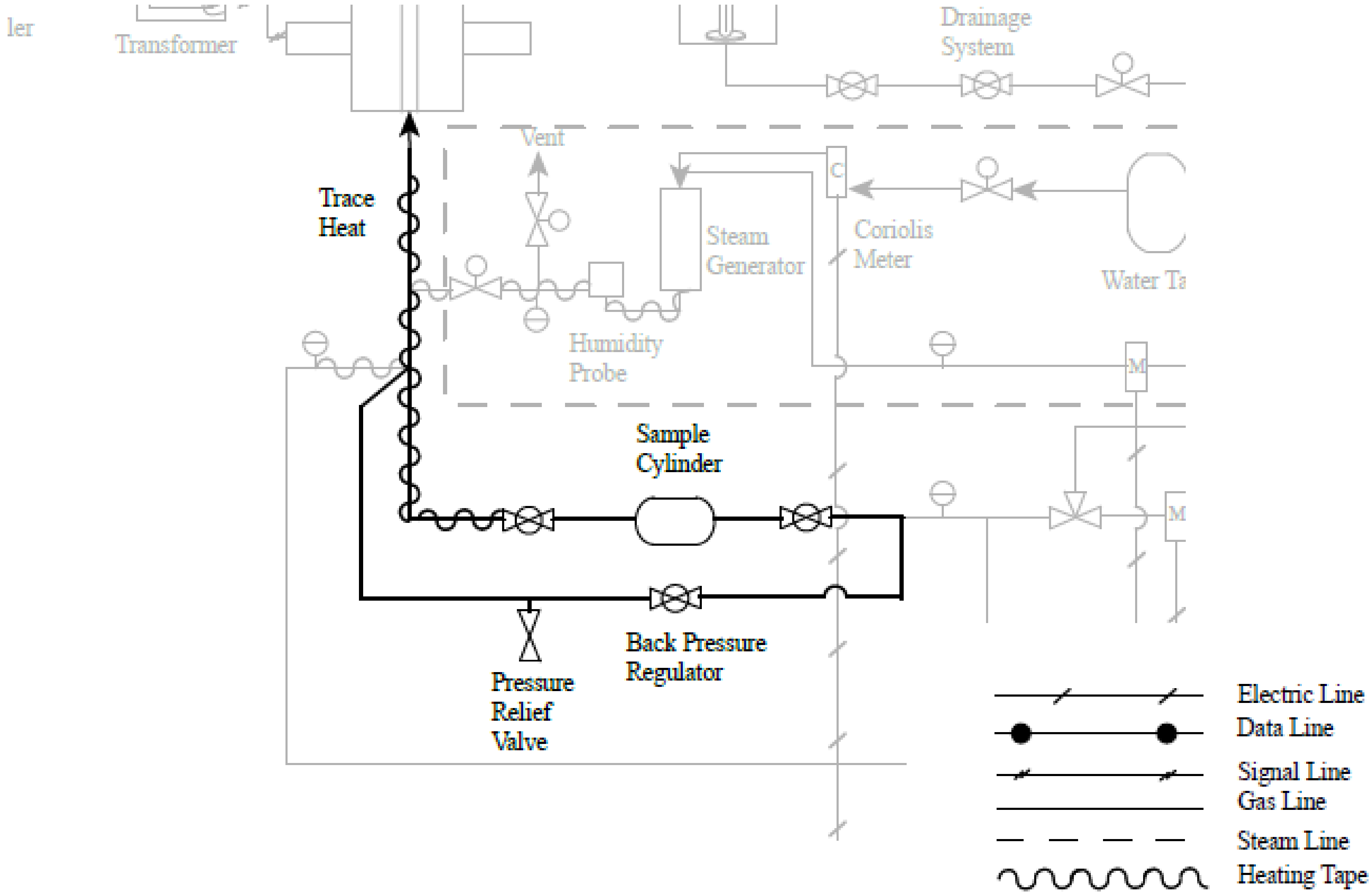
# Schematic of Rig: Feeding System



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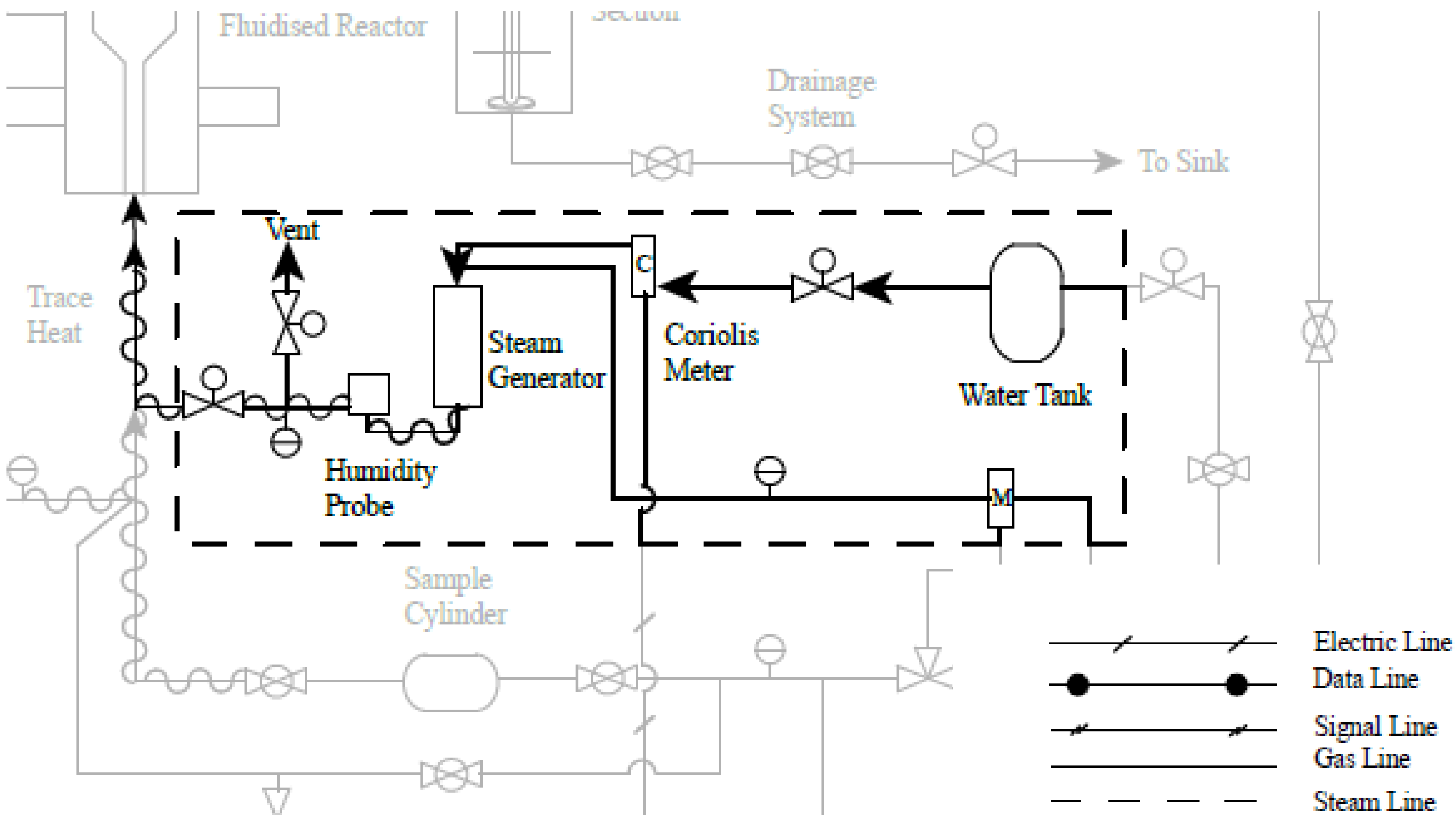
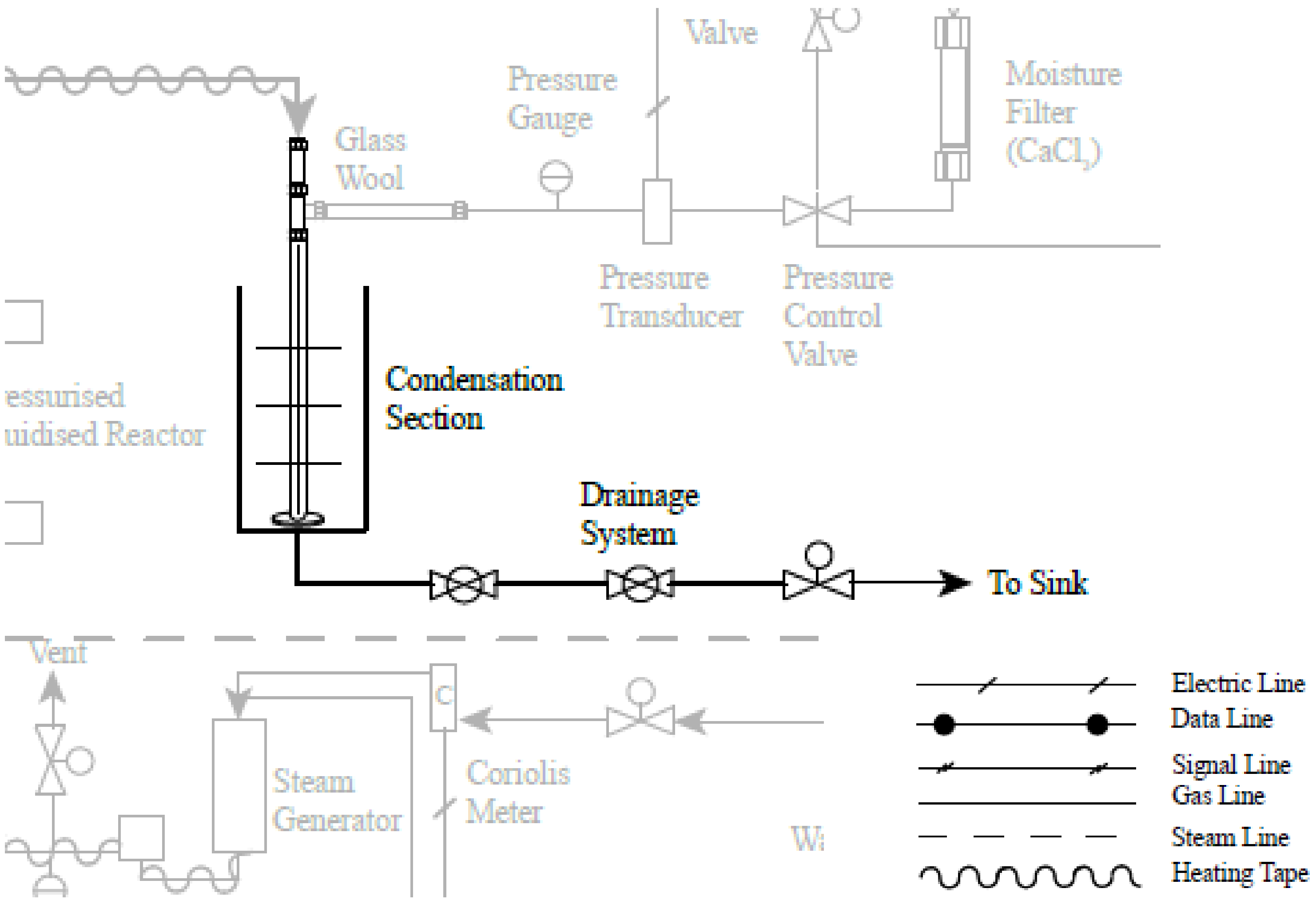
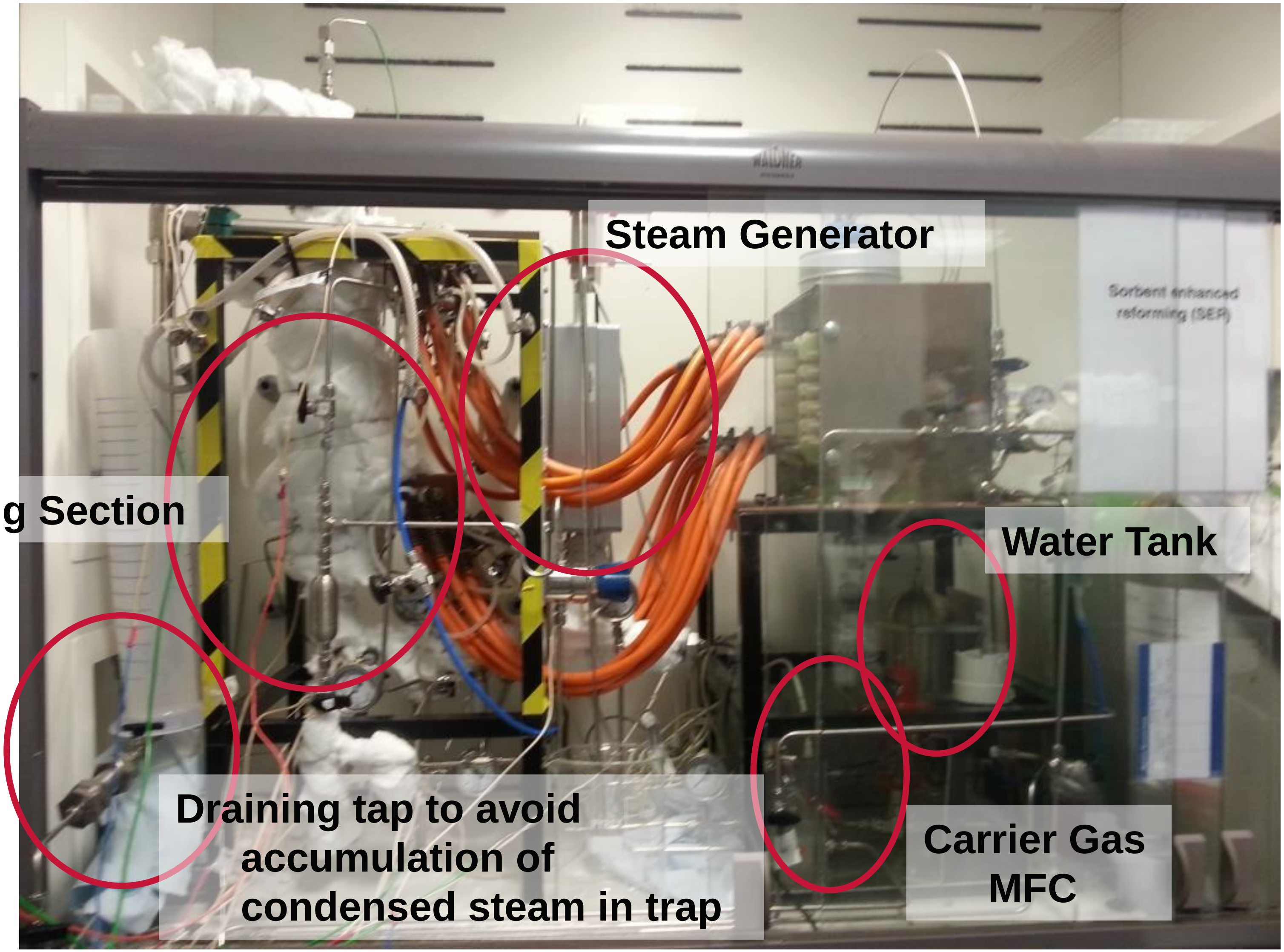
# Schematic of Rig: Steam Generation System



# Schematic of Rig: Steam Condenser



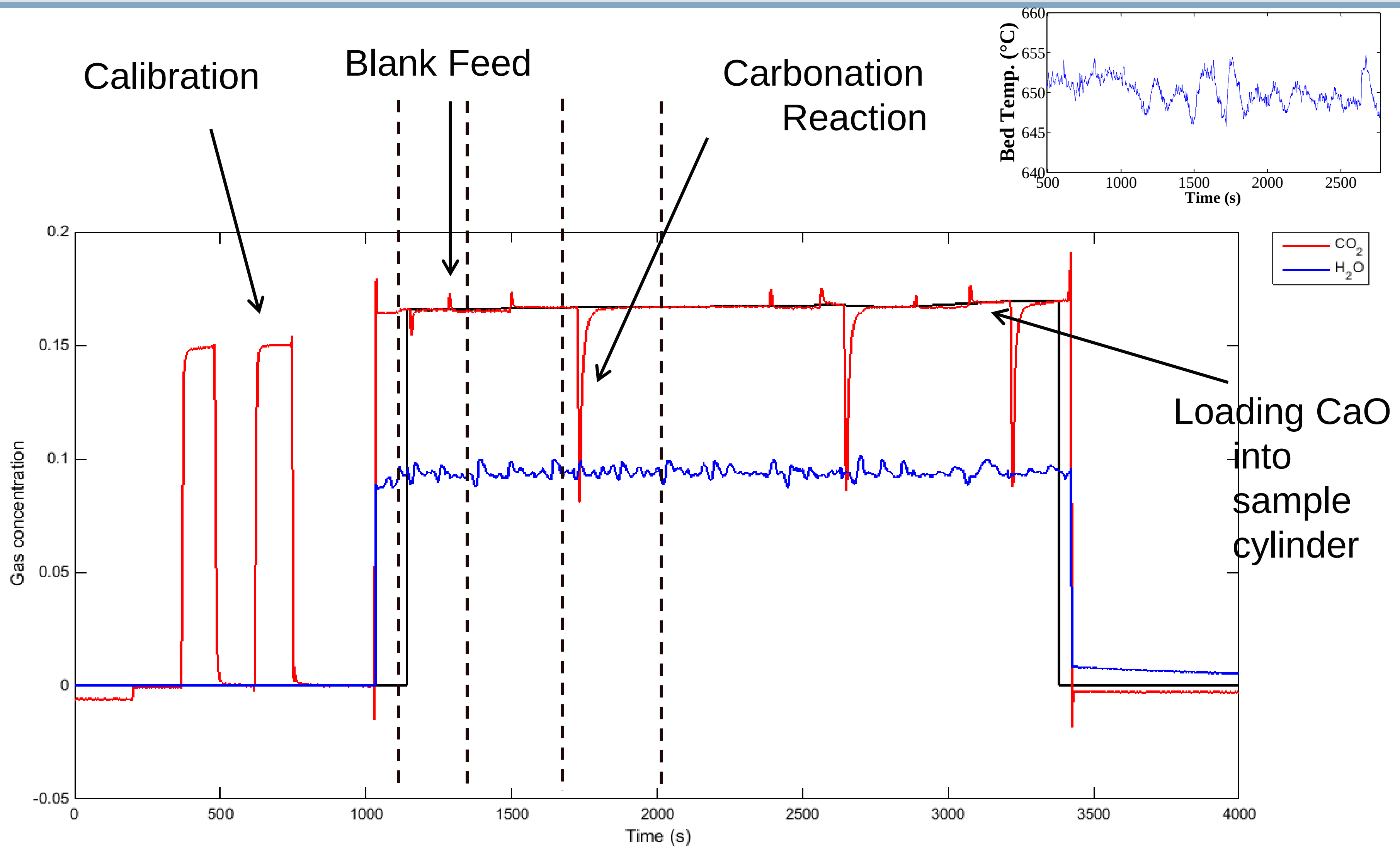
# Experimental Setup



# Brief Overview of Experimental Conditions

| Measurement | Value |
|---|---|
| Mass of Inert Bed (g) | 50 |
| $U/U_{mf}$ | 3 |
| Mass of CaO Sample (g) | 0.5 |
| Size of Sample (µm) | 355-425 |
| System Pressure Range (bara) | 1.5, 3, 5 |
| Bed Temperature Range (°C) | 550 - 750 |
| $CO_2$ Concentration Range (vol %) | 3.75 - 30 |
| Steam Concentration Range (vol %) | 3 - 10 |

# Typical Results from an Experiment at 650 °C, 1.5 bara, 15% $CO_2$ and 10% steam



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# Definition of the peak rates and reaction constants

Here, *r* is the peak rate (highest rate observed during the reaction), *k* is the rate constant and *n* is the order of reaction:

$$rate\ equation\ in\ terms\ of\ partial\ pressure\ of\ CO_2:$$

$$r = k\left(P_{CO_2} - P_{eq}\right)^n$$

$$r = \left[\frac{mol}{g.s}\right], k = \left[\frac{mol}{g.s.bar}\right],$$

$$P\ is\ the\ outlet\ concentration\ in\ [bar]$$

$$r' = rM_w \qquad r' = \left[\frac{1}{s}\right], \qquad M_w = 56.077\ g.mol^{-1}$$

$$k' = \frac{kRT}{S_g} \quad k' = \left[\frac{m}{s}\right]$$

$$S_g = specific\ surface\ area\ in\ \left[\frac{m^2}{g}\right]$$

# CHOOSING MASS OF SAMPLE

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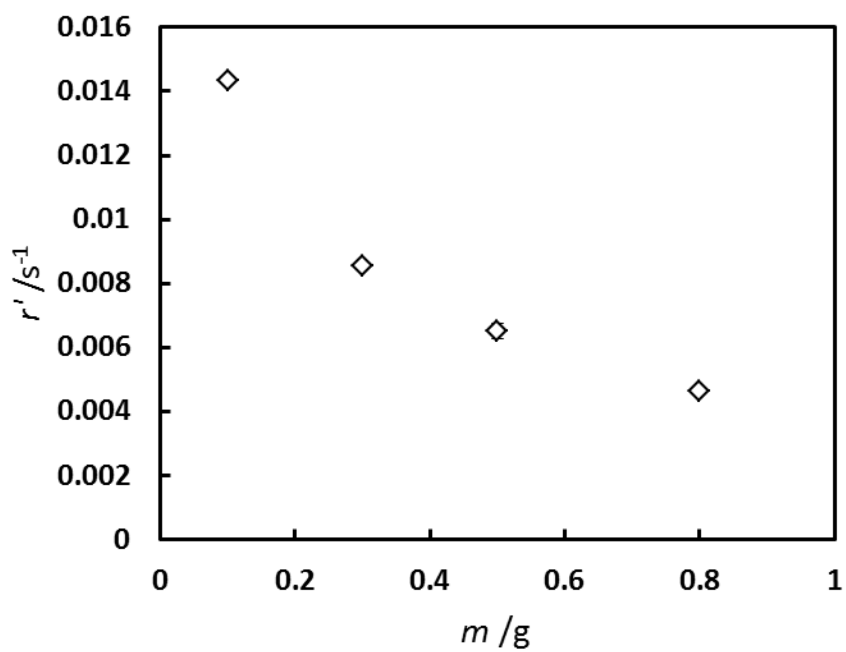
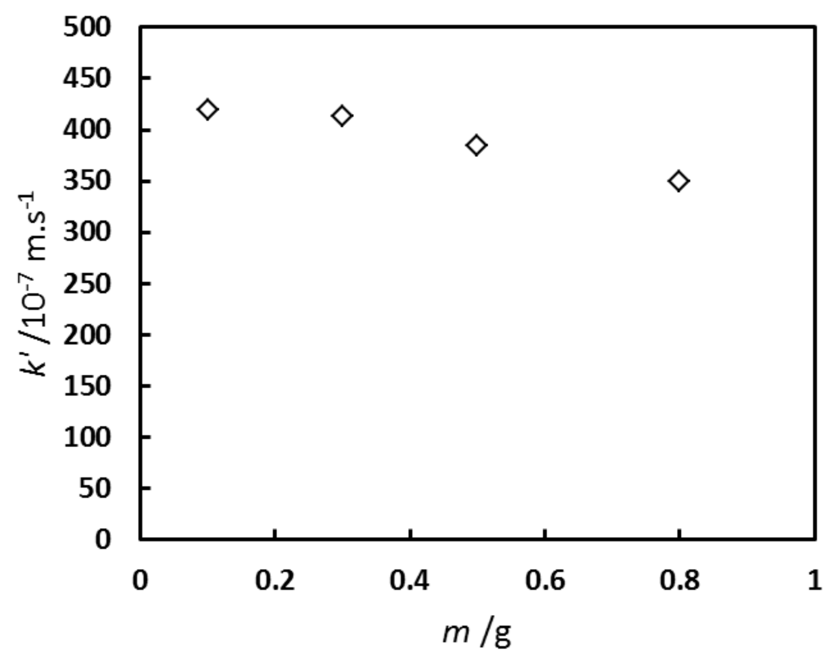
# Effect of varying the mass of sample without steam at 650 °C

The mass has been reduced until the rate constant is invariant while ensuring a good signal to error ratio




◇ 1.5 bara, 3.75% CO2, no steam, 650 °C




◇ 1.5 bara 3.75% CO2, no steam, 650 °C

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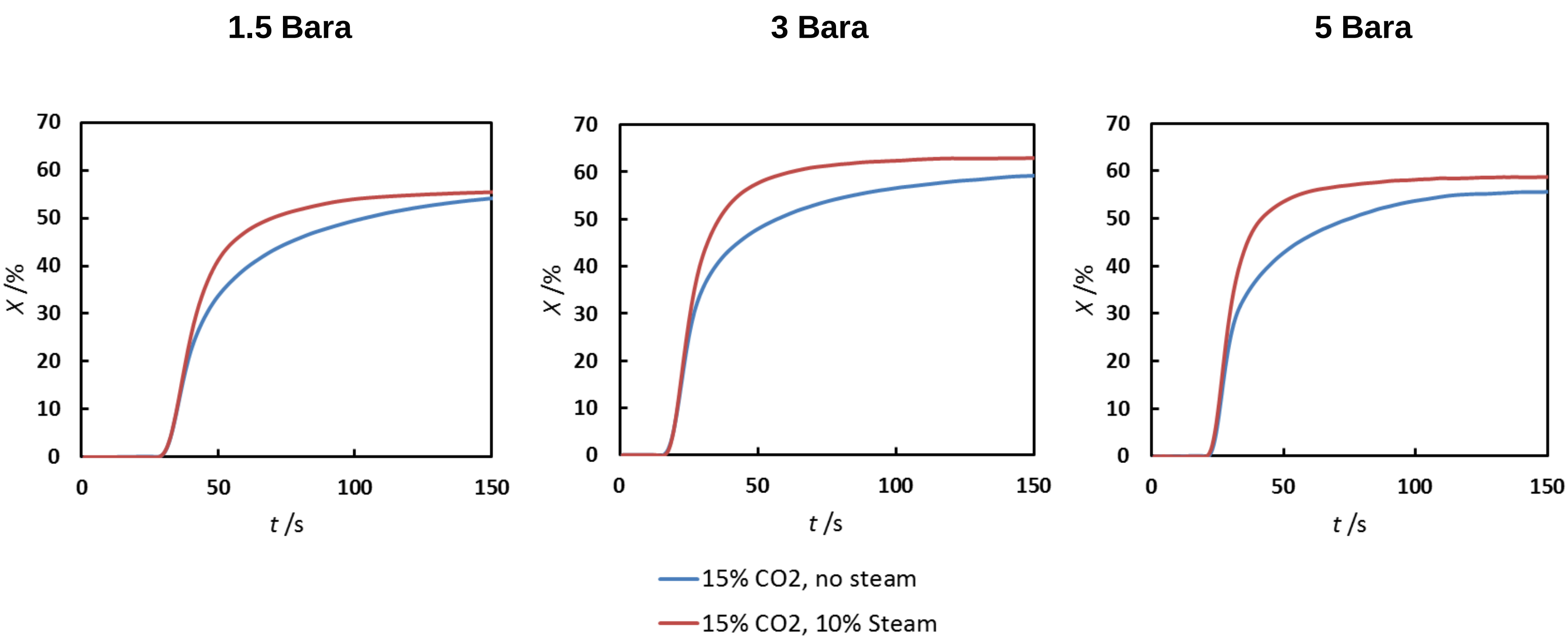
# Conversion vs time at 650 °C




*1. Arias, B., Grasa, G., Abanades, J.C., Manovic, V., and Anthony, E.J., The Effect of Steam on the Fast Carbonation Reaction Rates of CaO. Industrial & Engineering Chemistry Research, 2012.* ***51(5)****: p. 2478-2482.*

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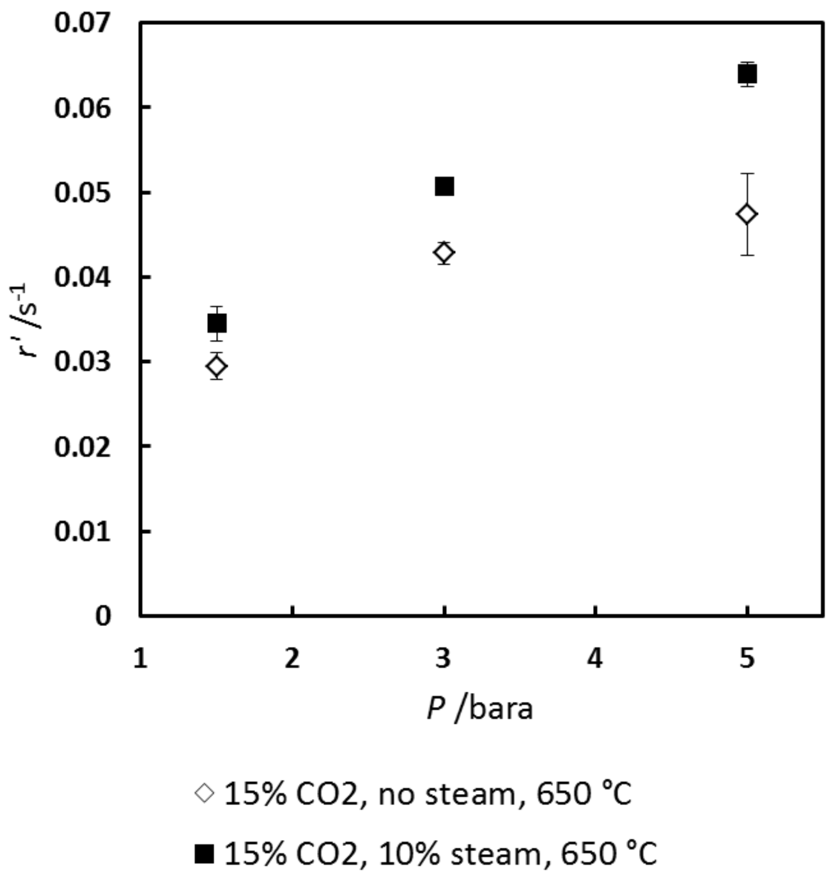
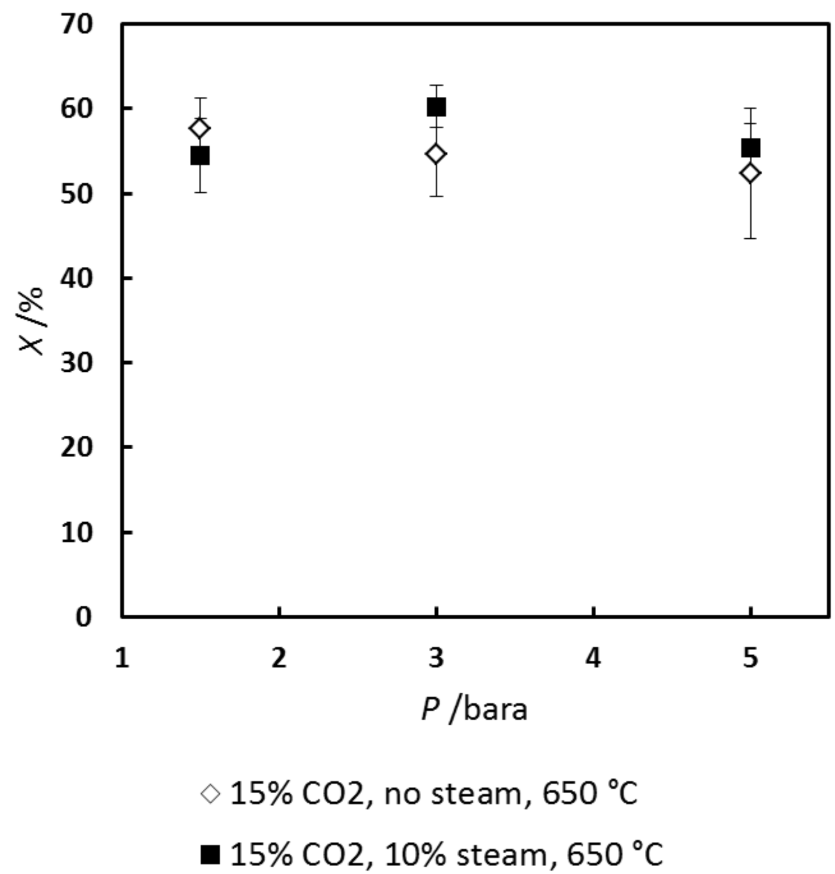
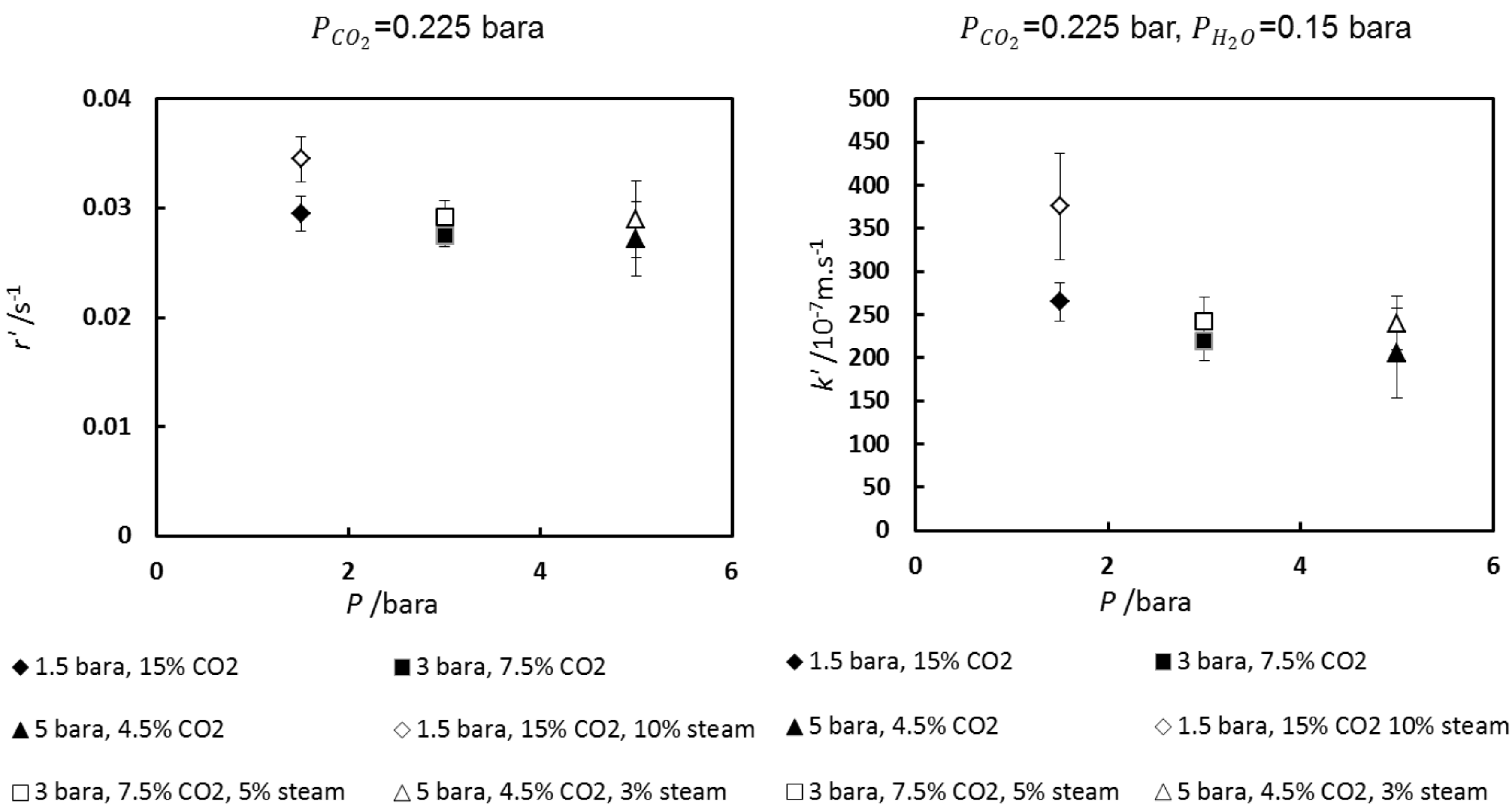
# Carbonation Experiments at different pressures with and without Steam at 650 °C



# EFFECT OF SYSTEM PRESSURE

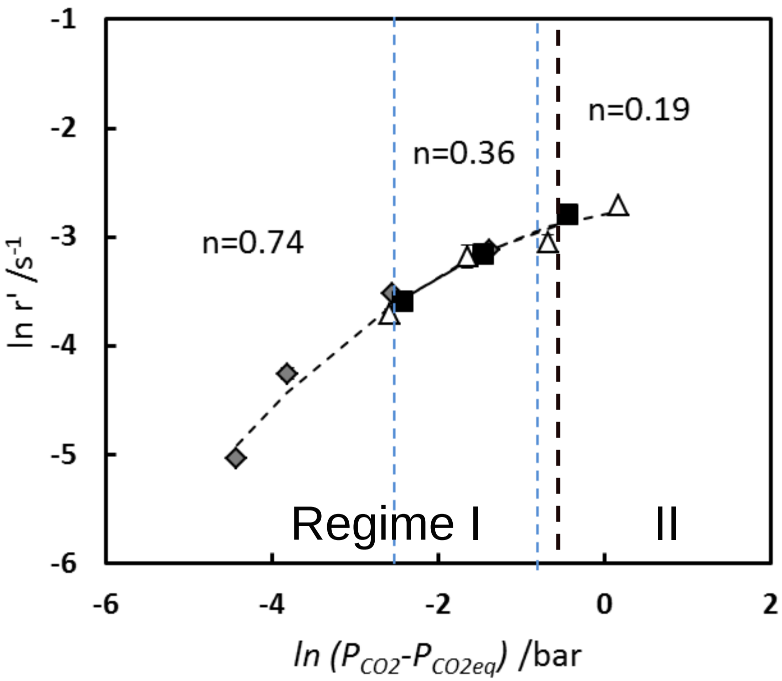
# Effect of changing the total system pressure



# EFFECT OF $CO_2$ CONCENTRATION

# Order of reaction: maximum rate method

**Without Steam**

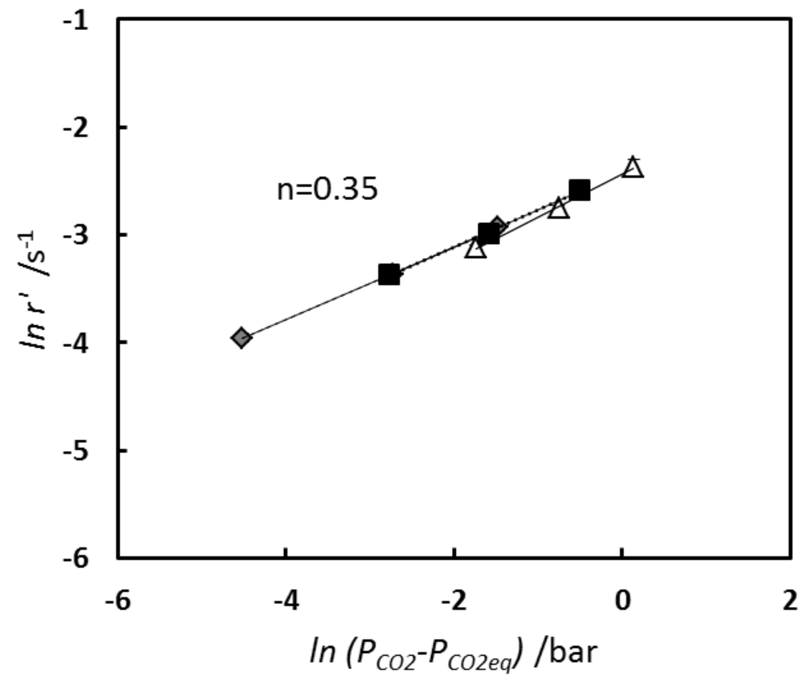



◆ 1.5 bara, no steam, 650 °C

■ 3 bara, no steam, 650 °C

△ 5 bara, no steam, 650 °C

**With Steam**




◆ 1.5 bara, 10% steam, 650 °C

■ 3 bara, 10% steam, 650 °C

△ 5 bara, 10% steam, 650 °C

*4 Yu F.C., Fan L.S.,, Kinetic Study of High-Pressure Carbonation Reaction of Calcium-Based Sorbents in the Calcium Looping Process (CLP), Ind. Eng. Chem Res., 2011, 50(20), pp11528-11536*

# DETERMINING THE INTRINSIC KINETICS FROM SIZE FRACTIONS

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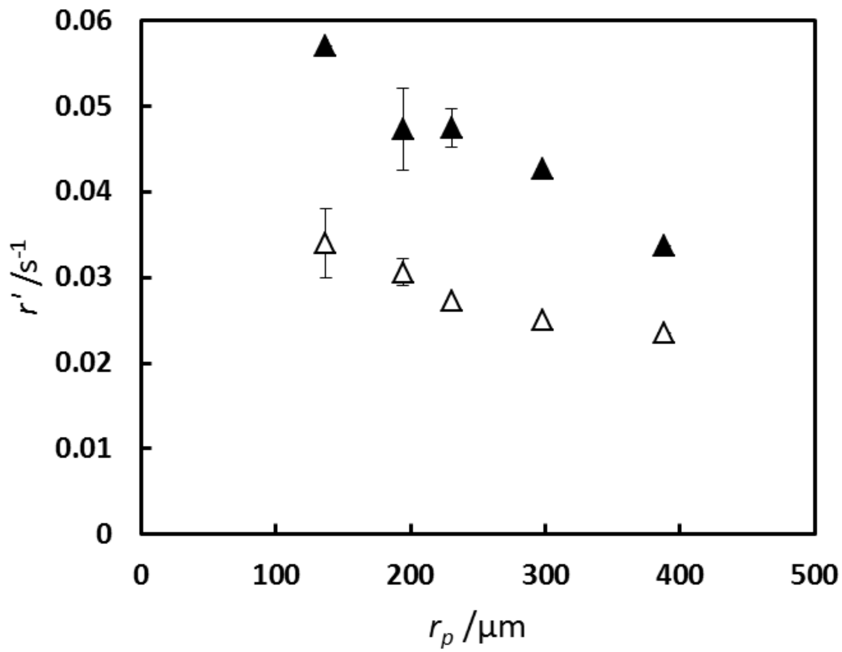
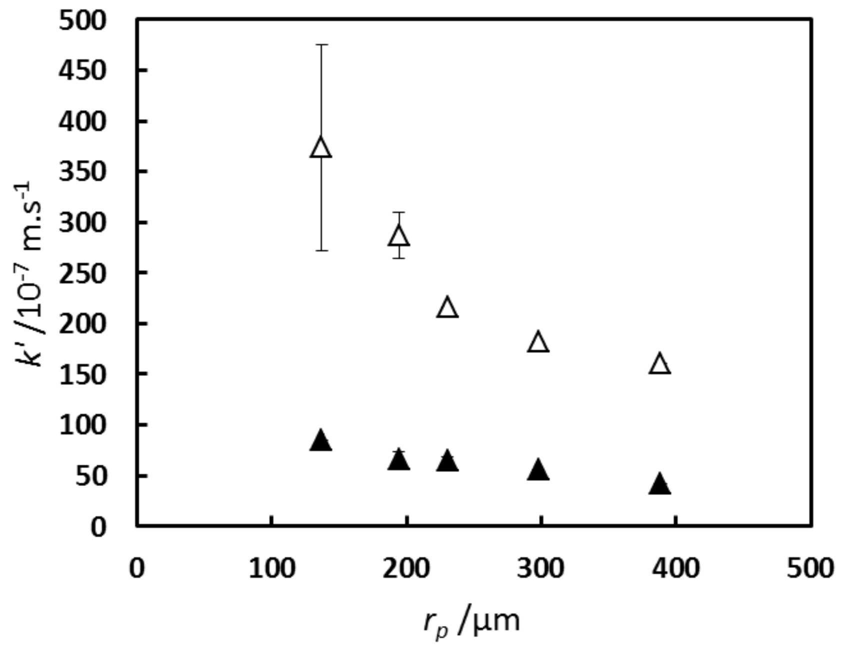
# Effect of varying the size fractions of CaO with and without steam at 650 °C




△ 1.5 bara, 15% CO2, no steam, 650 °C

▲ 5 bara, 15% CO2, no steam, 650 °C




△ 1.5 bara, 15% CO2, no steam, 650 °C

▲ 5 bara, 15% CO2, no steam, 650 °C

# Estimation of Intrinsic rate constant and effectiveness factor

*From a pseudo-steady state assumption, the rate of $CO_2$ entering a surface of spherical particles must be equal to the rate of the chemical reaction with in the particle. Assuming a first order irreversible reaction (usually true as the back concentration of $CO_2$ is low) in a porous particle:*

$$\mathbf{r}' = \mathbf{k}' C_{\mathrm{CO_2}} \qquad (1)$$

$$\frac{1}{\mathbf{k}'} = \frac{\mathbf{R}\boldsymbol{\rho}_{CaO}}{3\mathbf{k}_{\mathrm{g,CO_2}}} + \frac{1}{\boldsymbol{\eta}\mathbf{k}_i'}$$

*Also for a porous spherical particle, a mass balance of $CO_2$ within a spherical shell of the particle gives:*

$$\boldsymbol{\eta} = \frac{3}{\boldsymbol{\phi}^2}(\boldsymbol{\phi}\coth\boldsymbol{\phi} - 1) \qquad (2)$$

$$\boldsymbol{\phi} = \sqrt{\frac{\mathbf{k}_i'\boldsymbol{\rho}_{CaO}}{\mathbf{D}_{\mathrm{e,CO_2}}}}\mathbf{R}$$

$\mathbf{k}_\mathrm{i}'$ *and* $\boldsymbol{\eta}$ *could be solved iteratively by converging the effectiveness factor in equation (1) and equation (2) with an initial input of* $\boldsymbol{\eta} = 1$. $\mathbf{k}_{\mathrm{g,CO_2}}$ *and* $\mathbf{D}_{\mathrm{e,CO_2}}$ *need to be estimated first before the iteration.*

# Calculating Effective diffusivity

*The effective diffusivity, $\mathbf{D_e}$, in equation (2) was estimated from the bulk diffusivity, $\mathbf{D_b}$ (obtained from Chapman-Enskog kinetic theory)[5] and Knudsen diffusivity, $\mathbf{D_K}$ [6] with experimental data, and used $\boldsymbol{\tau}$ as a fitted tortuosity factor, which takes in account the effect of the tortuous path within the particle on the effective diffusivity*

$$\frac{1}{D_e} = \frac{\varepsilon_{CaO}}{\tau}\left(\frac{1}{D_K} + \frac{1}{D_b}\right) \quad (3)$$

$$D_b = 0.001858 \times \frac{\sqrt{T^3\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}^{1/2}}{P\sigma_{12}^2\Omega^{(1,1)*}} \quad (4)$$

$$D_K = 97 r_e \sqrt{\frac{T}{M}} = 194\frac{\varepsilon_{CaO}}{S_g \rho_{CaO}}\sqrt{\frac{T}{M}} \quad (5)$$

5. HIRSCHFELDER, J. O., CURTISS, C. F. & BIRD, R. B. 1954. Molecular theory of gases and liquids, New York. London ;, Wiley ; Chapman & Hall.

6. SATTERFIELD, C. N. 1980a. Heterogeneous catalysis in practice, New York ; London, McGraw-Hill.

# Calculating external mass transfer coefficient

*The external mass transfer coefficient,* $\mathbf{k_g}$*, in equation (1) was calculated using the definition of Sherwood number, and Sherwood number was estimated using a correlation* [7] *. The velocity of the gas, U, was calculated using a inlet flow rate of 55 ml/s (293K) and height of the bed of 11 cm:*

$$\mathbf{k_g = D_b Sh/d_p} \quad (4)$$

*Where*

$$\mathbf{Sh = 0.91 Re_p{}^{0.49} Sc^{0.33}} \quad (5)$$

$$\mathbf{Re_p = \rho_g U d_p/\mu} \quad (6)$$

$$\mathbf{Sc = \mu/(\rho_g D_b),} \quad (7)$$

*7. Perry, R.H. and Green, D.W., Perry's Chemical Engineers' Handbook seventh edition. 1997: McGraw-Hill, New York, USA.*

# Procedure for deriving intrinsic rate constant and activation energy

*Step 1: Calculate* $\mathbf{k_g}$. *Calculate* $\mathbf{D_e}$ *assuming* $\boldsymbol{\tau}$*=4*

*Step 2: Calculate* $\mathbf{k}_i'$ *and* $\boldsymbol{\eta}$ *in equation (1) (First loop assuming* $\boldsymbol{\eta}$*=1)*

*Step 3: Using the* $\mathbf{k}_i'$ *and* $\mathbf{D_e}$ *Calculated earlier to estimate a new value of* $\boldsymbol{\eta}$ *in equation (2)*

*Step 4: Calculate* $\mathbf{k}_i'$ *and* $\boldsymbol{\eta}$ *in equation (1) using the new value of* $\boldsymbol{\eta}$

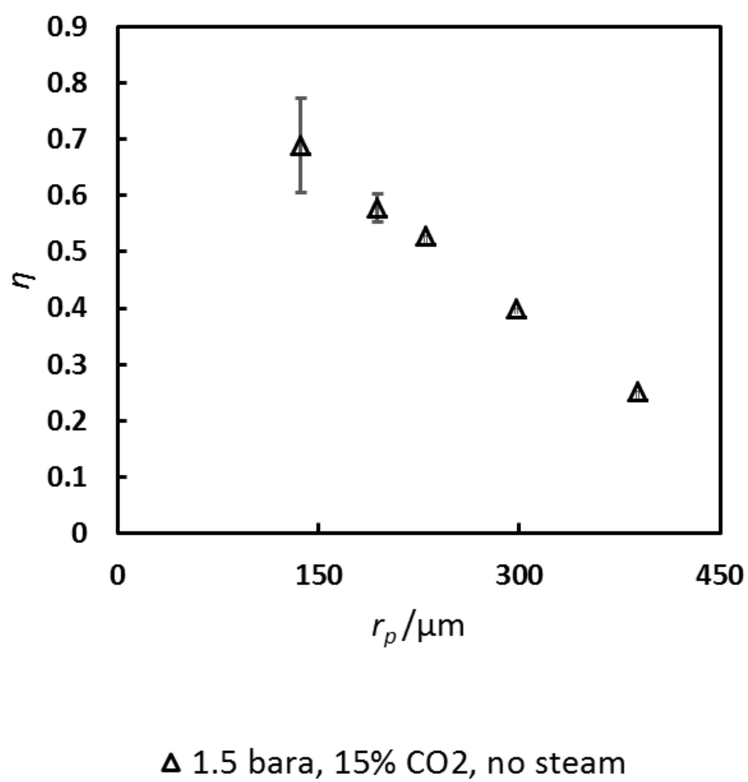
*Step 5: Repeat step 2 to step 4 until* $\boldsymbol{\eta}$ *converge*

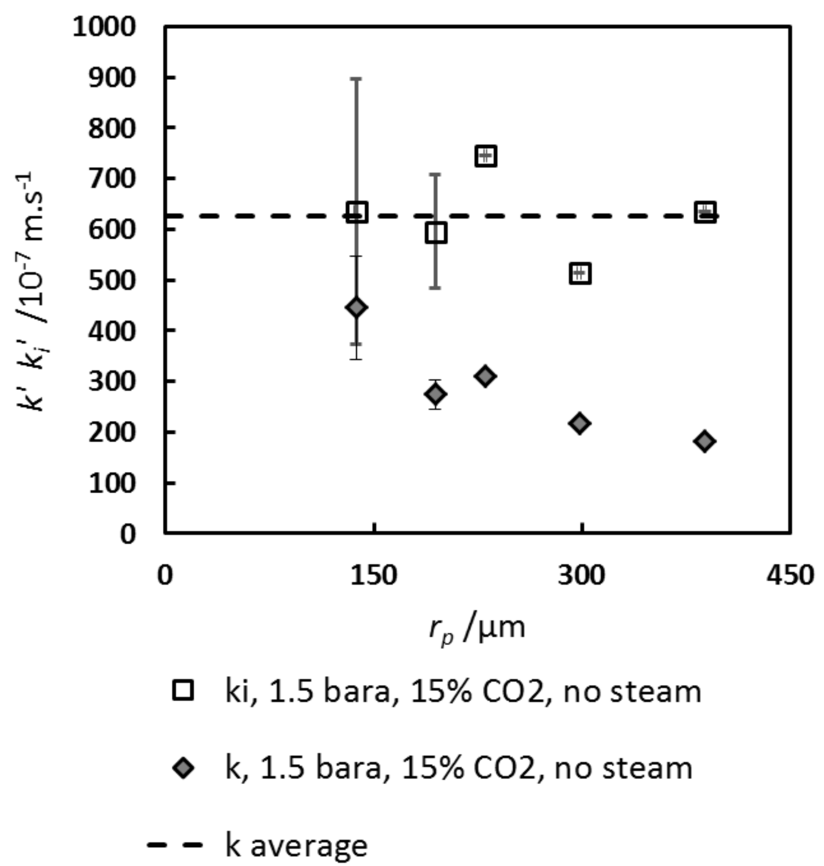
*Step 6: Adjust value of* $\boldsymbol{\tau}$ *(and therefore* $\mathbf{D_e}$*) so that same* $\mathbf{k_i'}$ *is recovered for particles with different sizes at a single temperature.*

*Step 7: Assume the same* $\boldsymbol{\tau}$ *when deriving* $\mathbf{k}_i'$ *and* $\boldsymbol{\eta}$ *for other temperatures using step 2 to step 5*

*Step 8: Derive activation energy E and pre-exponential factor A for reaction.*

# Effectiveness factors and intrinsic rate constants



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# EFFECT OF TEMPERATURE

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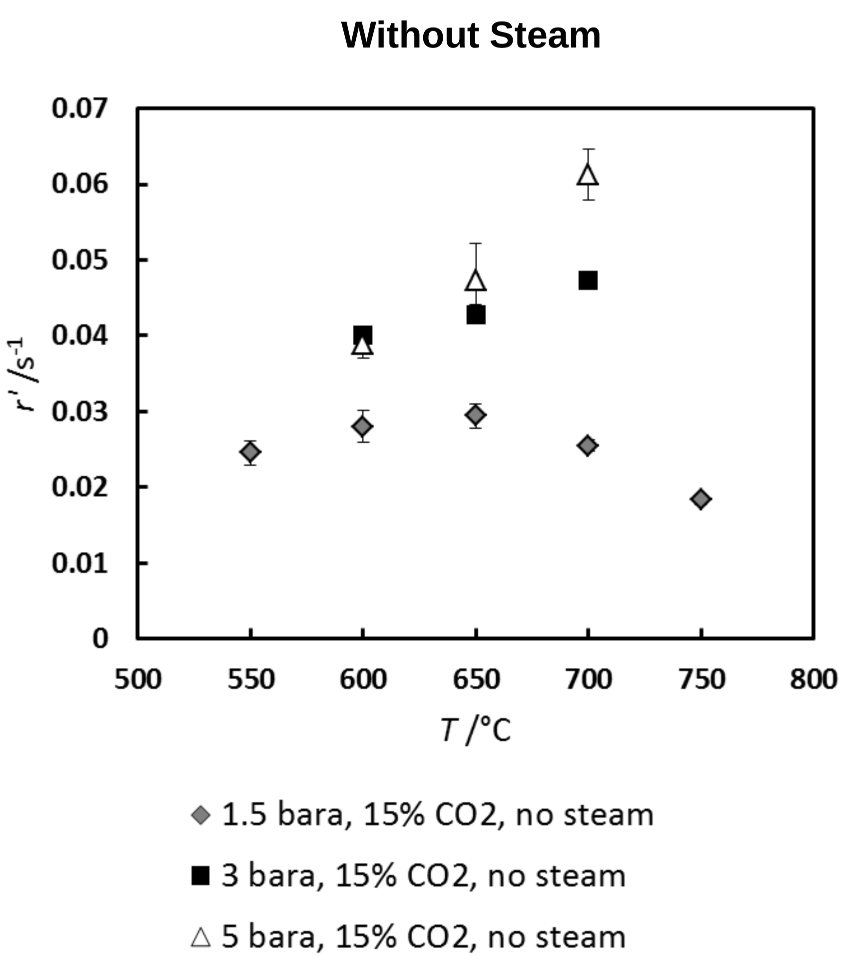
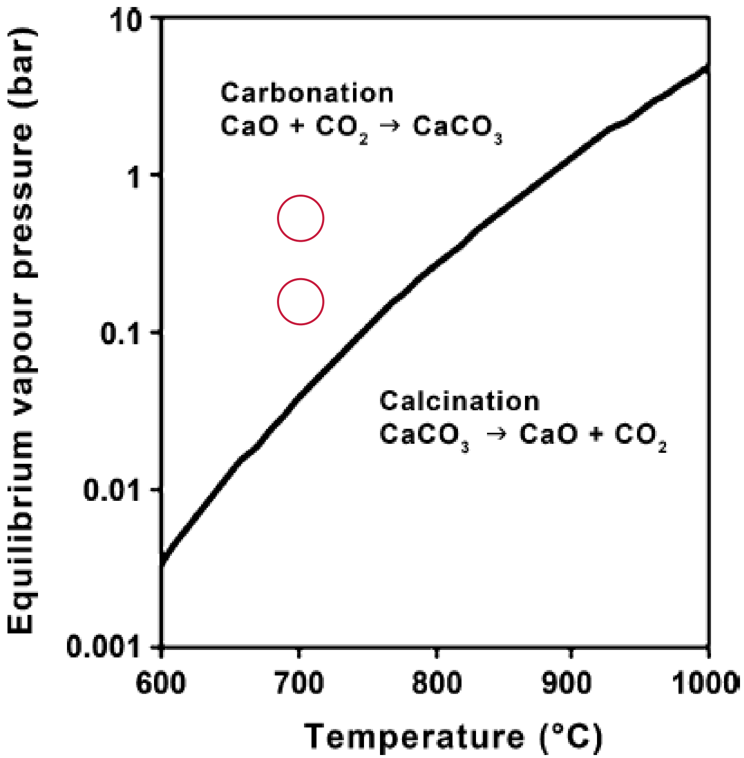
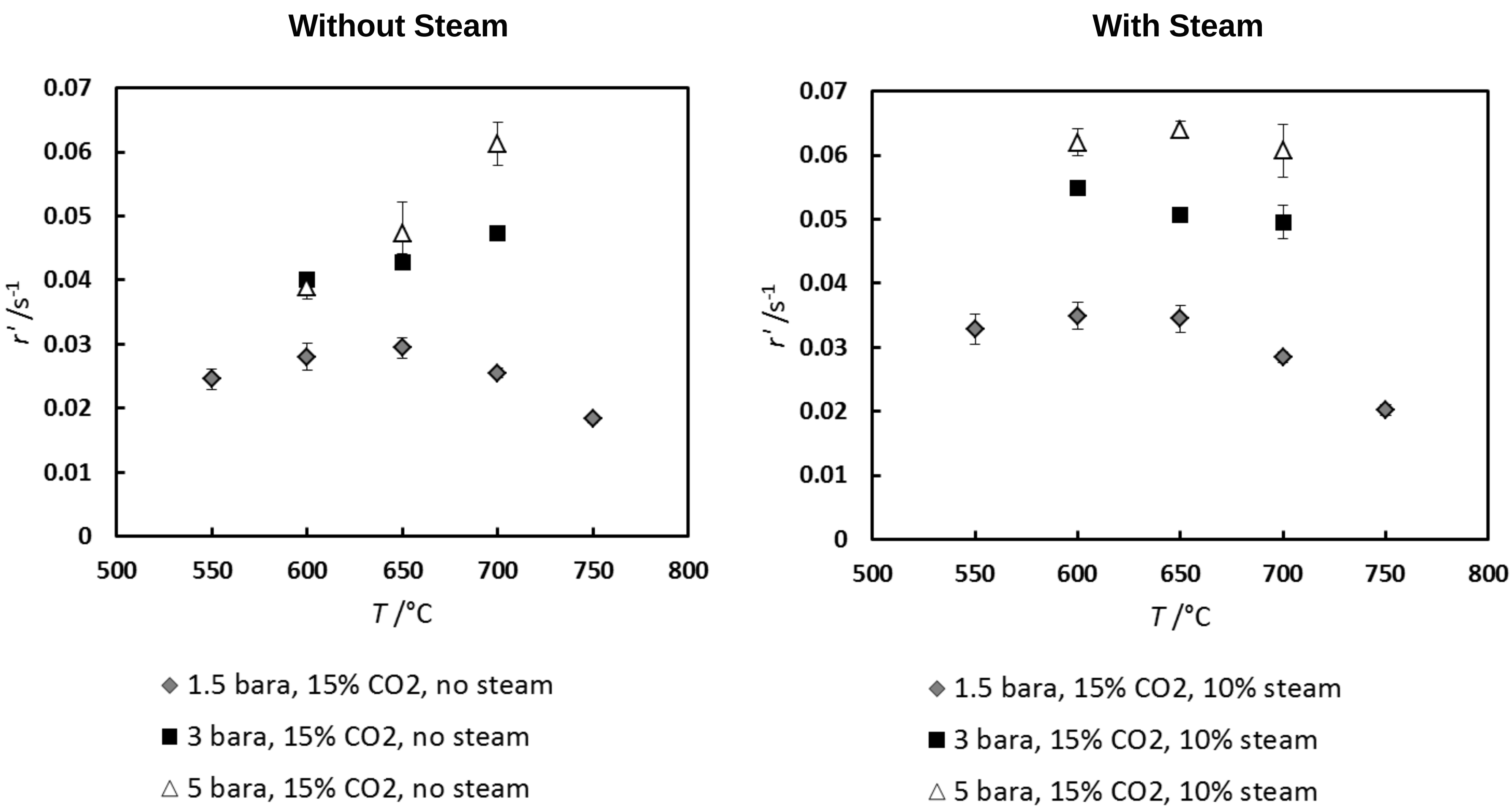
# Carbonation at different Temperatures with and without steam: Comparison of Observed Rates



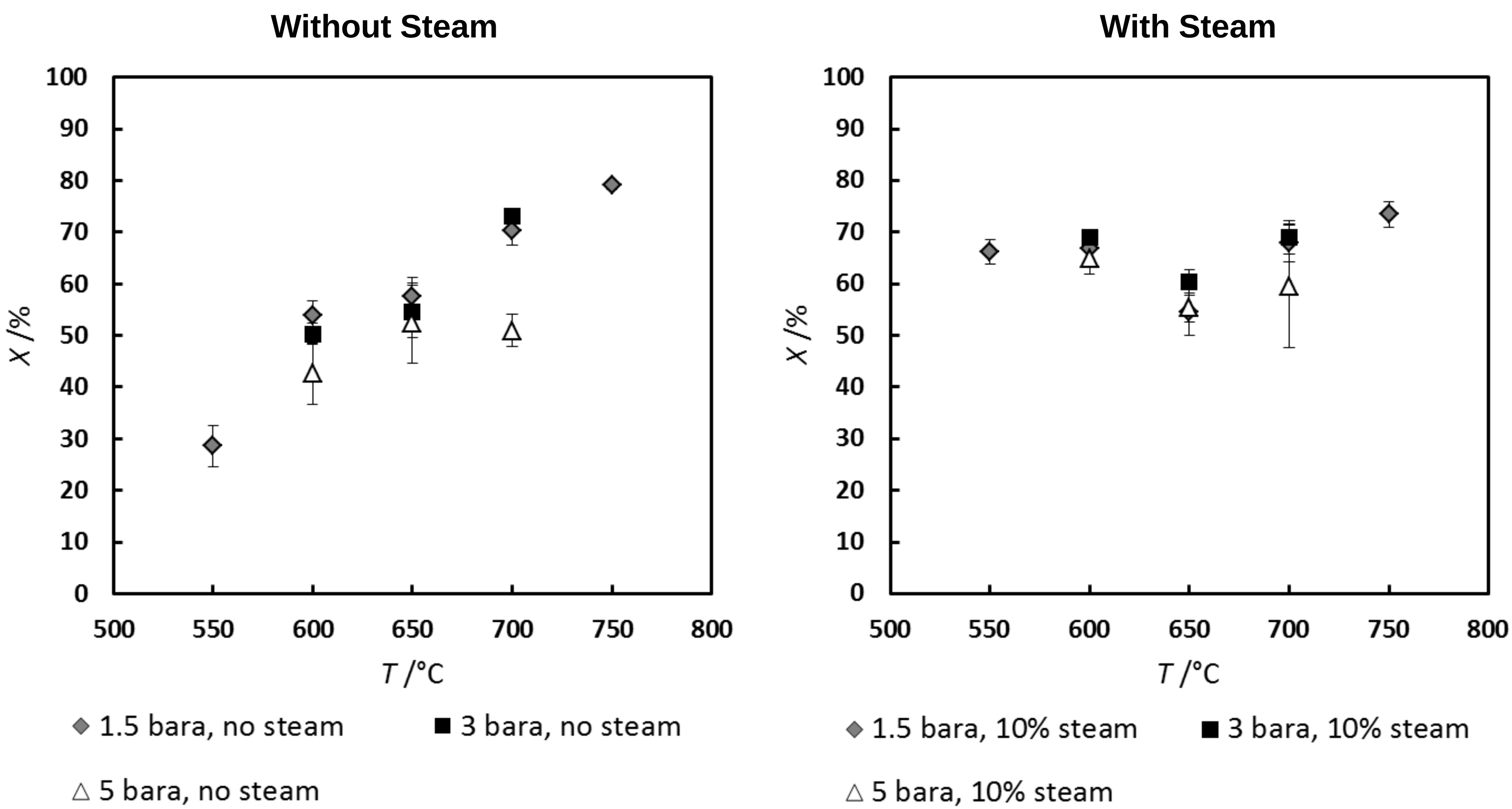




*7. J. Blamey, E. J. Anthony, J. Wang and P. S. Fennell, The Calcium Looping Cycle for Large-scale CO2 Capture, Prog Energ Combust, 2010, **36**, 260-279*

# Carbonation at different Temperatures with and without steam: Comparison of Observed Rates



# Carbonation at different Temperatures with and without steam: Comparison of Conversions




*Improvement in final conversion for lower temperature carbonation reactions in the presence of steam is also seen by Manovic and Anthony[3]

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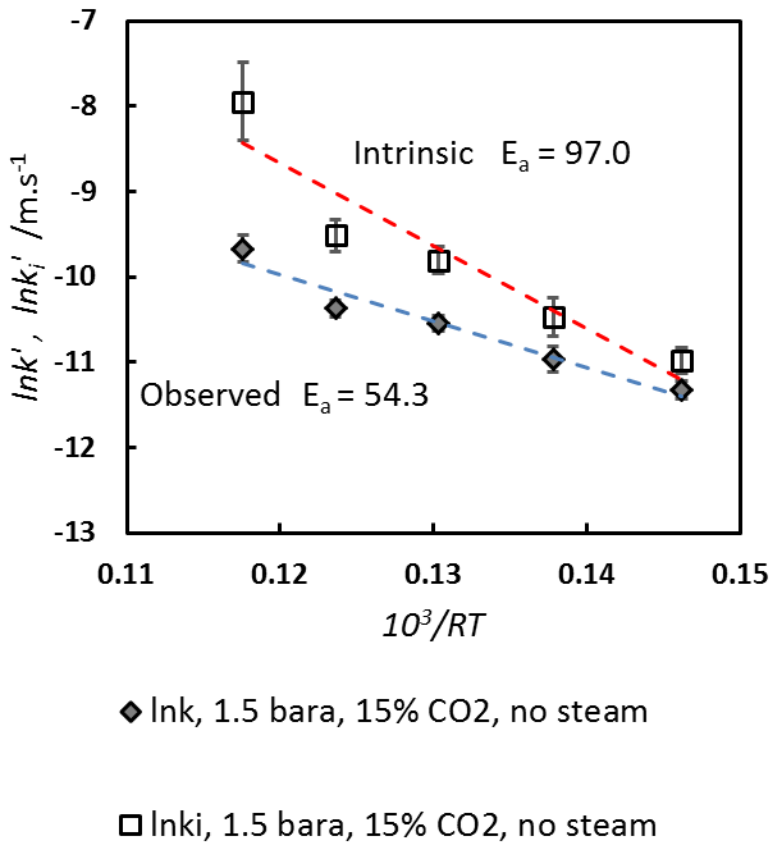
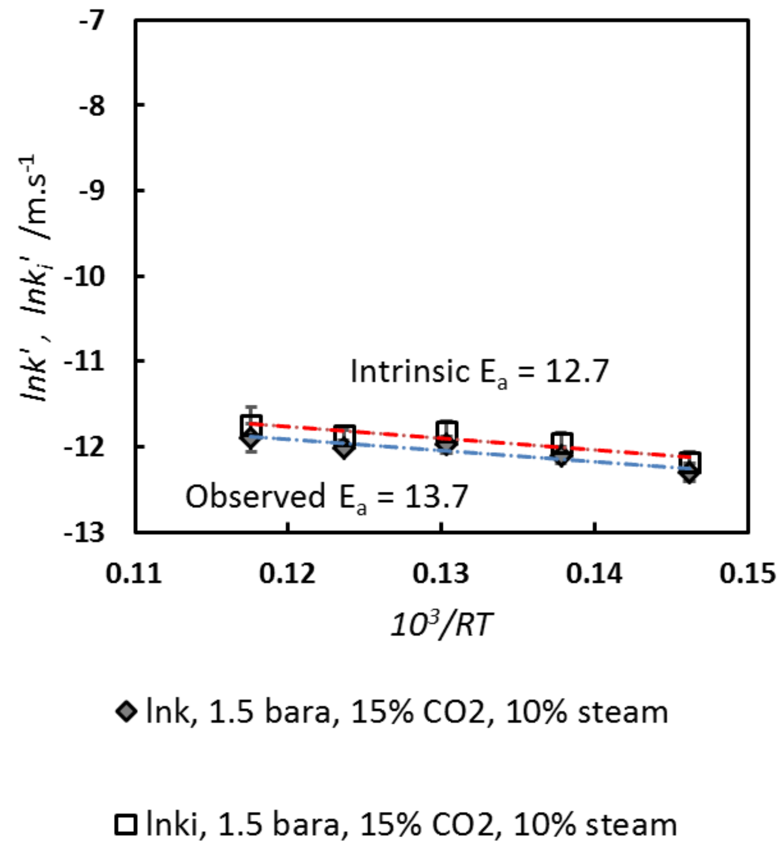
# Activation Energies and the effect of intrinsic kinetics

**Without Steam (1st Order Reaction)**




**With Steam (Order of reaction: 0.35)**




*The mechanisms of the reactions are being looked into to improve the accuracy of the rate constants

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# Summary

- The presence of steam has been shown to increase the observed rate of reaction
- Changing the system pressure does not have much of an impact on the observed reaction rate
- Higher rates are achieved by increasing the partial pressure of $CO_2$. The reaction order appears to change as the partial pressure of $CO_2$ increases
- Steam appears to improve the degree of carbonation at low temperature conditions
- Higher pressures allow faster carbonation rates at higher temperatures

# Acknowledgements

We gratefully acknowledge funding from the EPSRC for the PhD Studentship

Calix Calix

DECC Department of Energy & Climate Change

EPSRC Engineering and Physical Sciences Research Council

UKCCS RESEARCH CENTRE

Research Councils UK Energy For a Low Carbon Future

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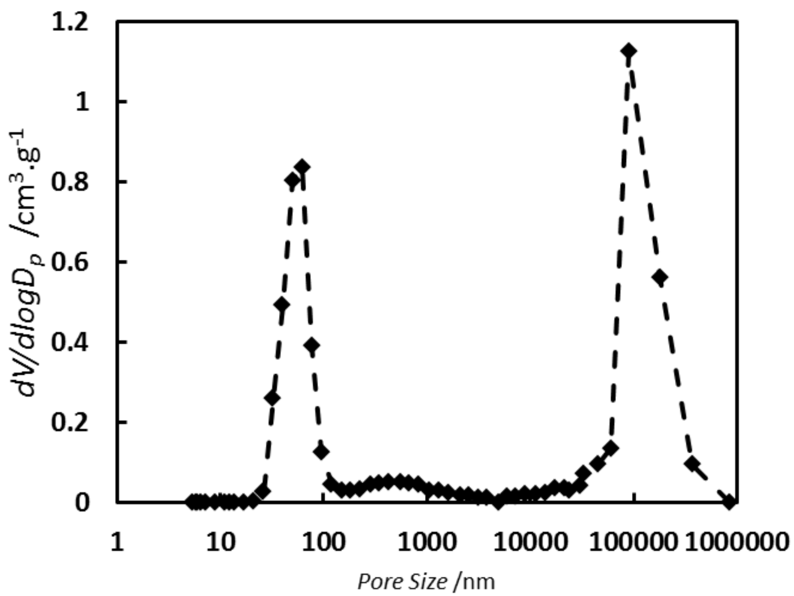
# Thank You for Listening
# Q&A

Email: p.fennell@imperial.ac.uk

# Supporting Slide 1: MIP Pore size distibrution

All pore sizes




Pore sizes <10 µm (discounting the interstitial voids)