

Investigating the performance of Fe- based oxygen carriers for pressurised chemical-looping combustion of gaseous fuels

**Zili Zhang^a, Joseph Yao^a, Matthew Boot-Handford^a, Nick Florin^a, Stuart Scott^b,
Paul S. Fennell^{a*}**

p.fennell@imperial.ac.uk

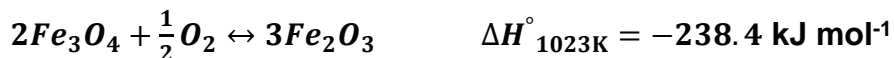
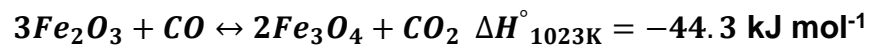
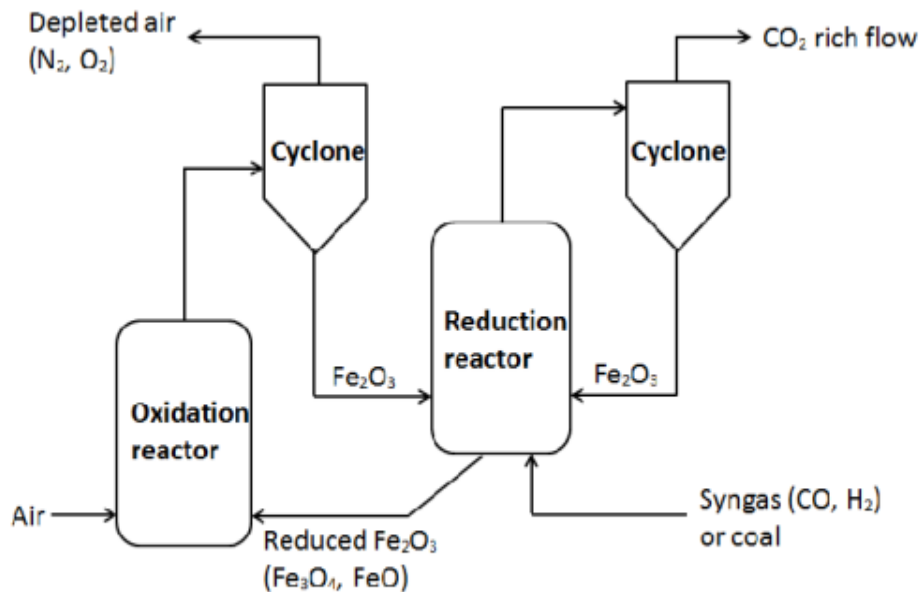
^aDept. of Chemical Engineering and Chemical Technology
Imperial College London

^bDepartment of Engineering, University of Cambridge

Presentation Overview

- Introduction to Chemical-Looping Combustion (CLC) and preparation of oxygen carrier materials.
- Kinetic studies of reduction of Fe_2O_3 -based particles with CO in a 3kW fluidised bed reactor at high temperature and elevated pressure.
- Analysis of Intrinsic kinetics of unsupported and supported Fe-based particles
- Reaction model for the iron-based oxygen carriers and validation using a idealised and complete fluidised bed model
- Conclusions.

Chemical-looping Combustion process (CLC)



CLC is a promising technology for power/heat generation with inherently integrated carbon capture.

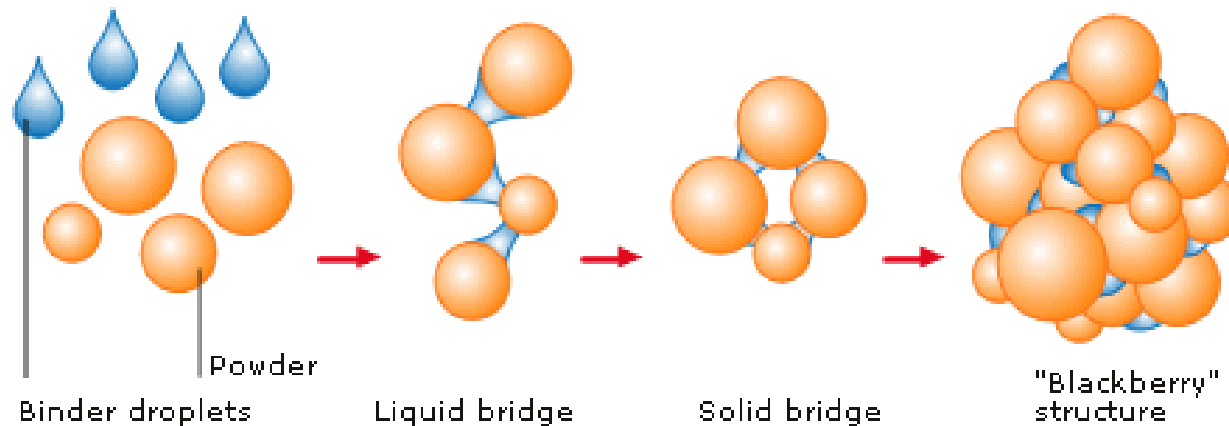
The common oxygen carriers (OCs) (Fe-, Cu-, Ni-, Mn-based). OCs can either be used pure or supported on a porous, inert material. Supported OCs typically offer robust and stable performance.

Successful implementation of CLC requires robust oxygen carriers.

Pressurisation is required for gas CLC in order to compete with the exergetic efficiency of the natural gas combined cycle plants (NGCC).

Intrinsic kinetics of the reduction of the oxygen carriers are key for fundamental study of the process.

Wet granulation techniques



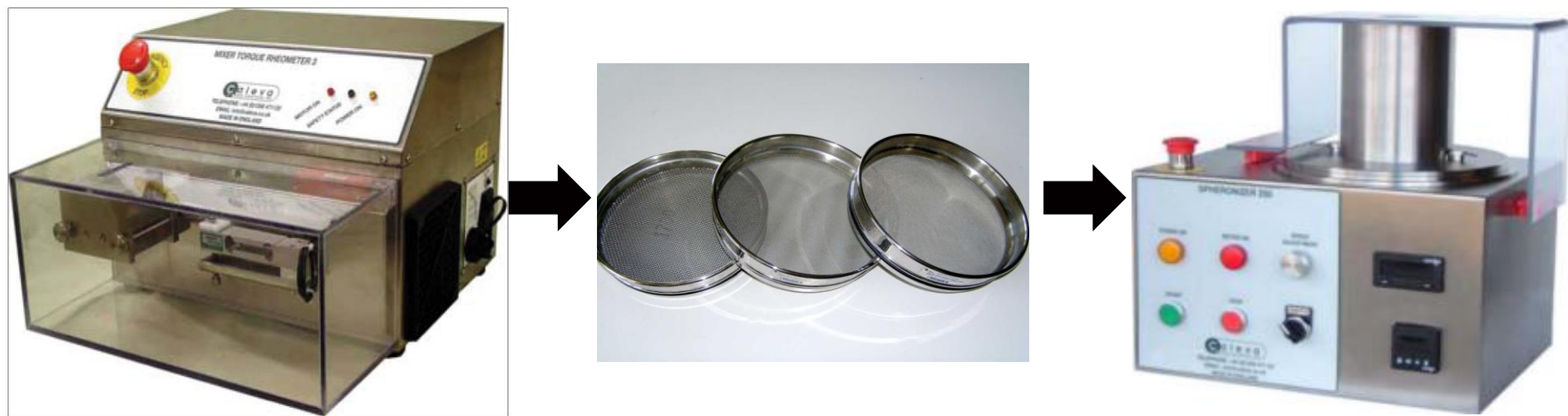
Two types of particles were prepared for initial trials:

- 100 wt.% Fe_2O_3 5 μm powder (Sigma Aldrich) (100Fe)
- 60 wt.% Fe_2O_3 5 μm powder and 40 wt.% Al_2O_3 powder (60Fe40Al)

The particles were prepared via a simple wet granulation technique from Fe_2O_3 powder and Al_2O_3 precursor ($\text{Al}(\text{OH})_3$ (Sigma Aldrich)) powders.

Fe_2O_3 and Al_2O_3 are cheap, widely available, non-toxic and environmentally benign.

Mixing and Sieving method (S)



Steps: High shear mixing while wet granulation (powder + DI water) → Sieving (wet paste) → granulation (wet particles) → Calcination at 900°C for 3 hours(dry particles)

- Use sieving and granulation to regulate the size and shape of the particles.
- Production capacity (~50g)
- Require more DI water during mixing.

Surface morphology (SEM analysis)

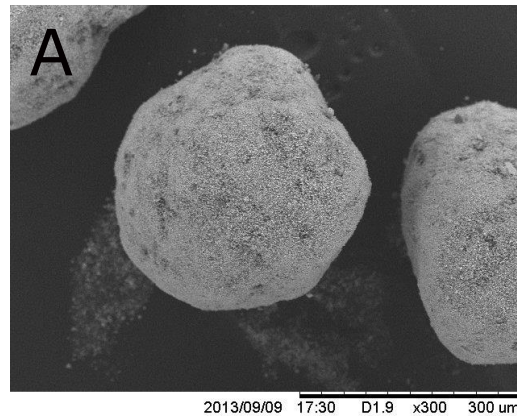


Figure 6: SEM images for 100Fe particles; A: 100Fe(S)

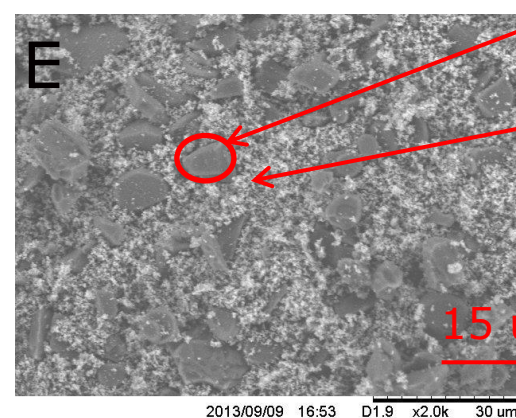
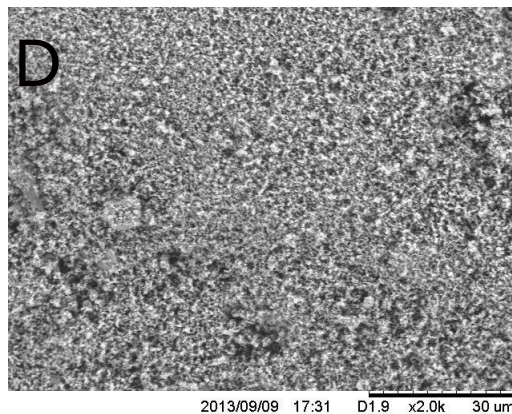
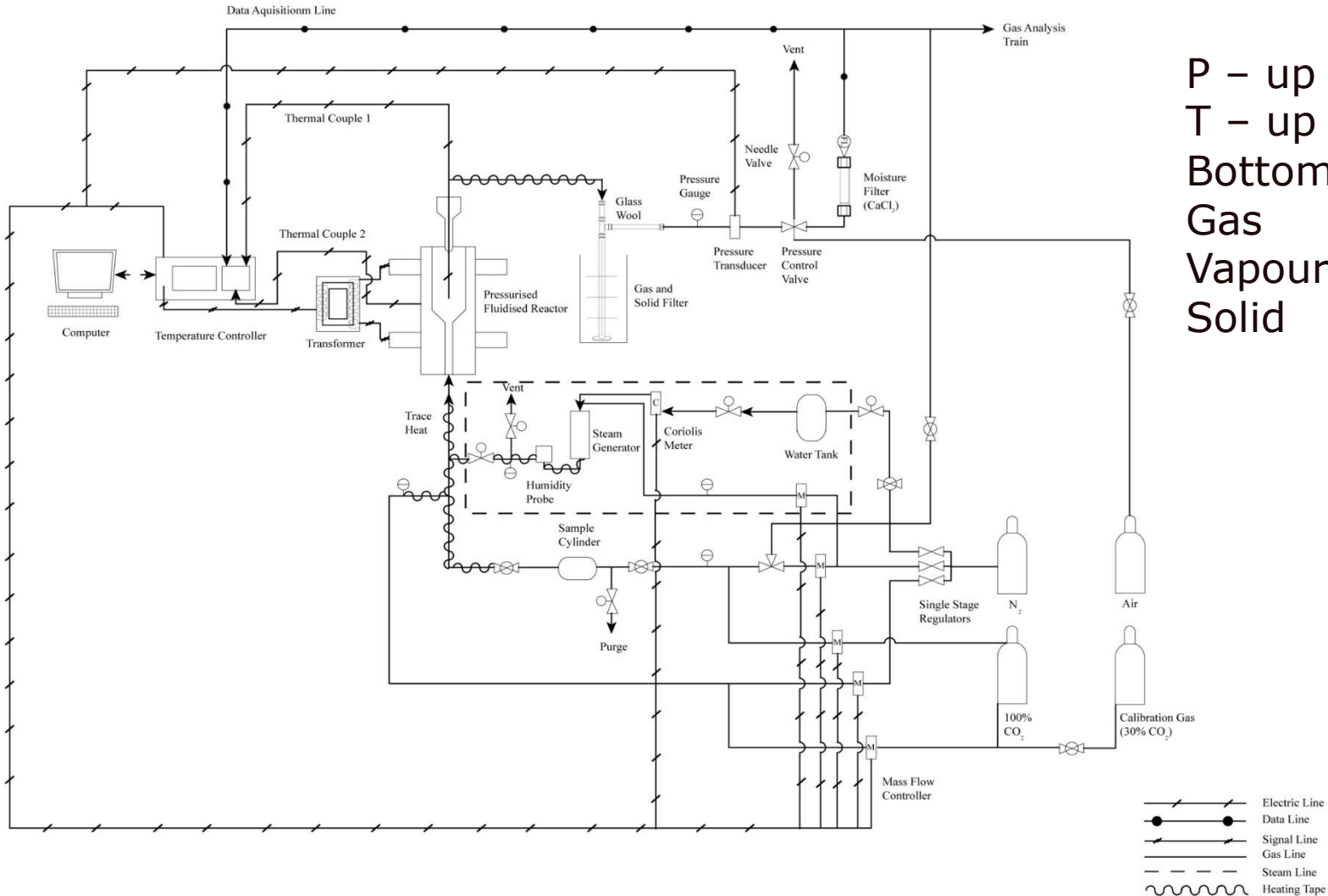


Figure 7: SEM images of surface morphology of : D: 100Fe(S), E: 60Fe40Al(S)

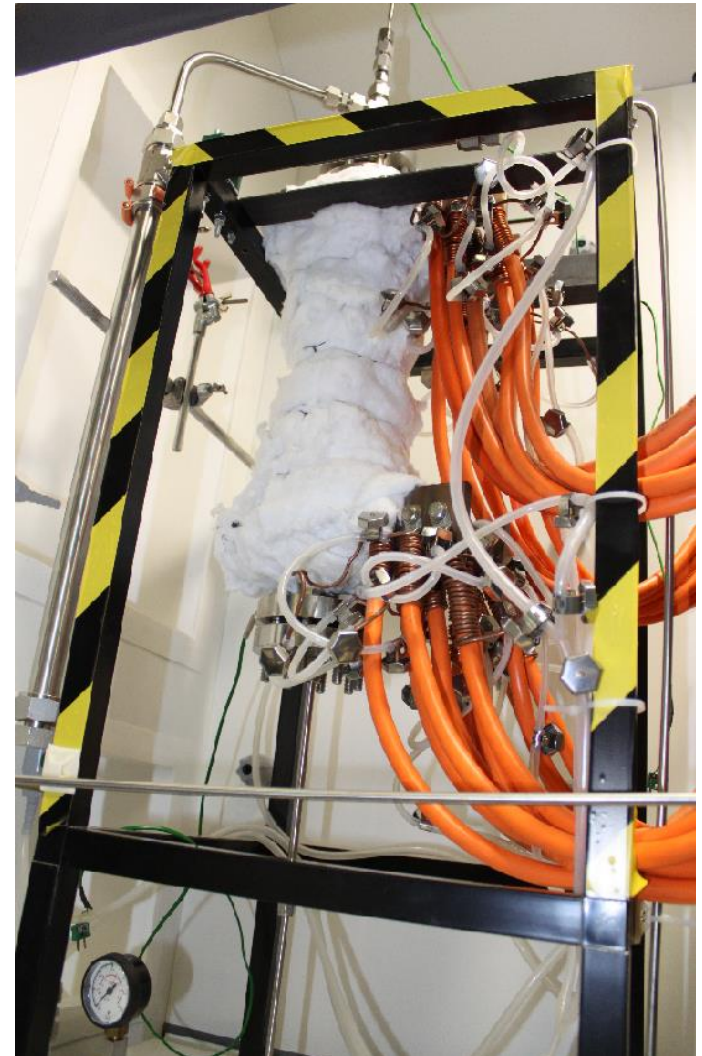
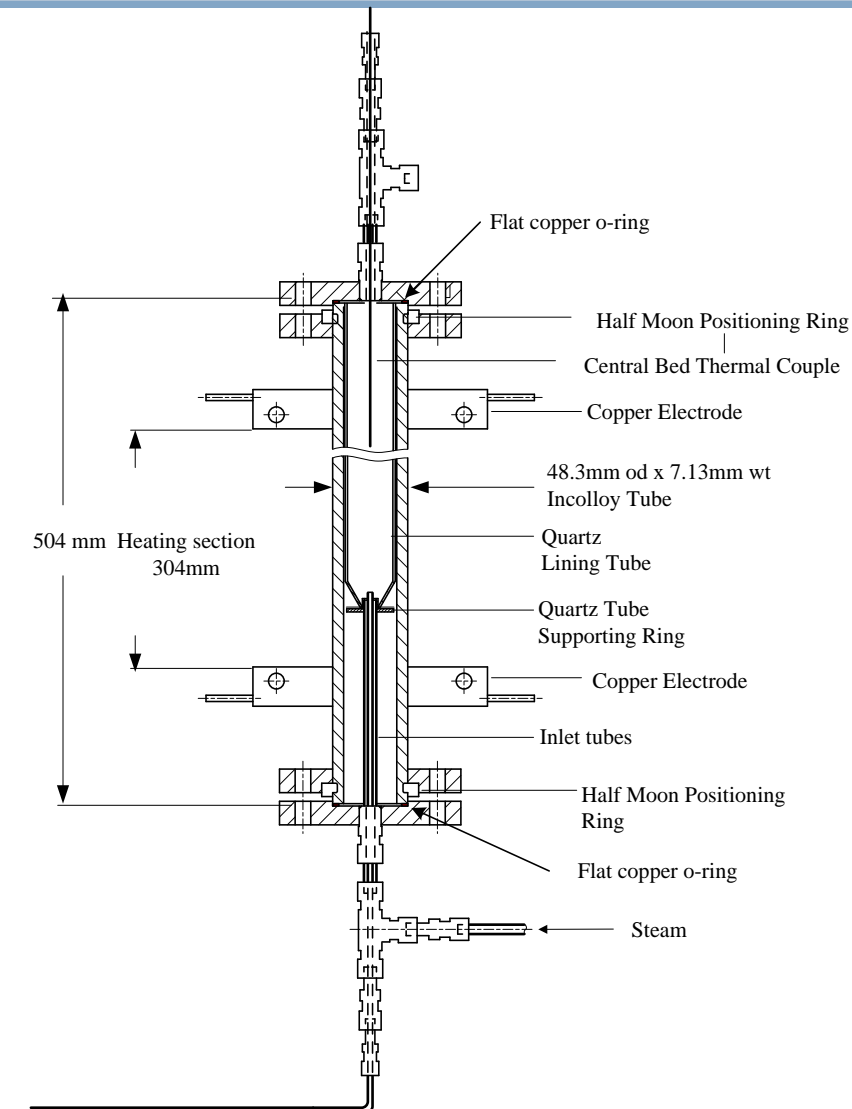
Kinetic studies of Fe_2O_3 -based particles in a 3kW fluidised bed reactor

Schematic diagram of a spouted (Fluidised) bed reactor system



P – up to 20 bar
T – up to 950 °C
Bottom injection:
Gas
Vapour
Solid

Detail of the closed spouted(Fluidised) Bed Reactor

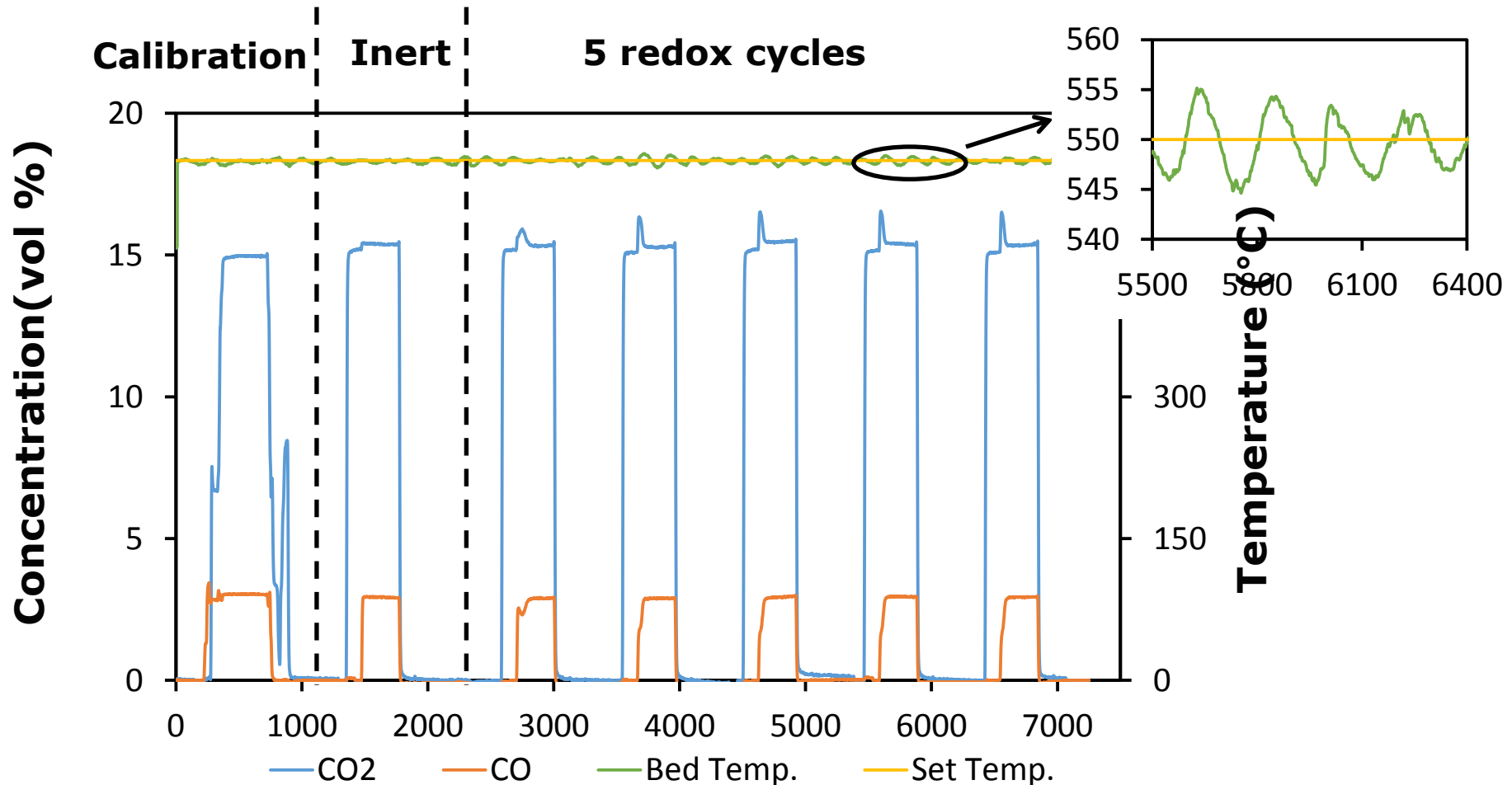


Investigation of kinetics of Iron oxide reduction with CO

Sample	Sample selection	Sand bed selection	T	P	F	Reduction gas	Oxidation gas
100Fe*		40g(500-710 μ m)		1.5bara			
	0.5g(300-425 μ m)		773-973K		2.5U _{mf}	N ₂ +CO+CO ₂ (80-85%, 1-5%, 15%)	N ₂ +Air(82%, 18%)
60Fe40Al2 (Al(OH) ₃ precursor)		40g(420-500 μ m)		1.5-5bara			

*The Fe₂O₃ particle was prepared by wet granulation of Fe₂O₃ power (5 μ m, Sigma-Aldrich > 99.9wt. %) in a high shear mixer before sintered at 900 °C

Typical cycles profile of 60Fe40Al reduction with CO at 823 K, 1.5bar



Derivation of the rates of the reaction

The concentration was de-convoluted according to:

$$c_P = c_{out} + \tau_{mix} \frac{dc_{out}}{dt}$$

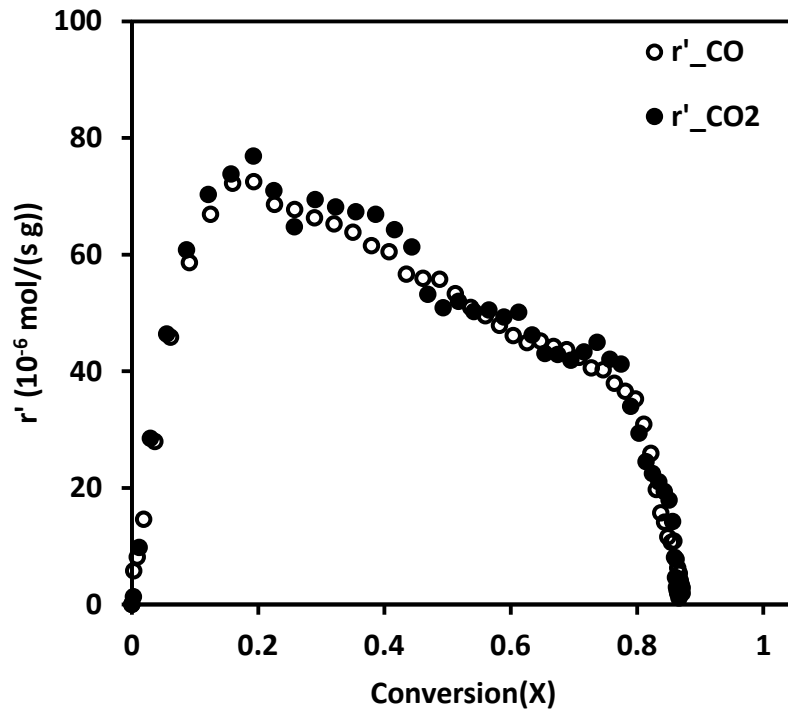
τ_{mix} was estimated using a published method by Fennell et al.*

The de-convoluted concentration was taken as instantaneous concentration in the particulate phase, i.e., c_P , assuming fast cross flow between the two phases of the fluidised bed

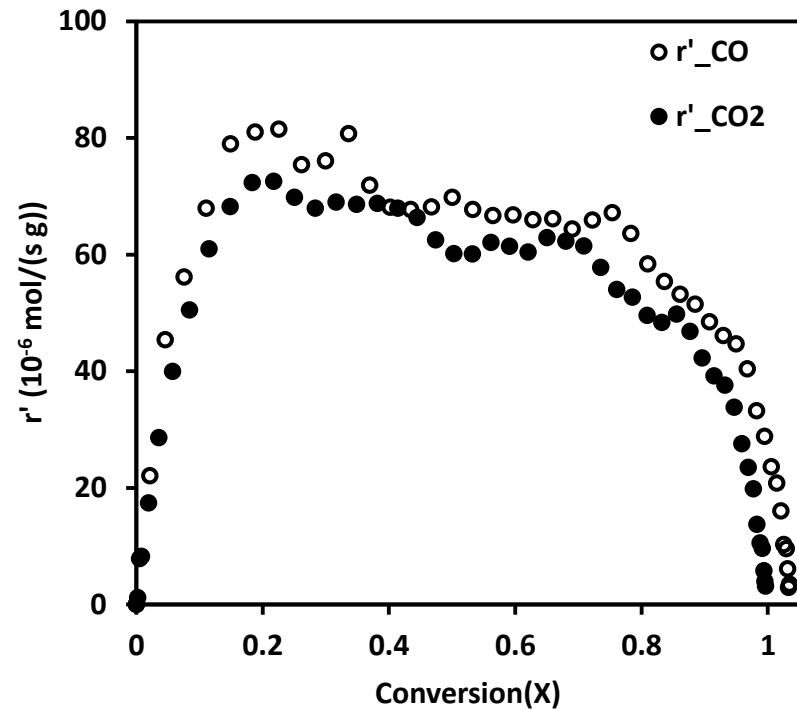
*Fennell, P.S., Dennis, J.S., Hayhurst, A.N., 2009. The order with respect to oxygen and the activation energy for the burning of an anthracitic char in O₂ in a fluidised bed, as measured using a rapid analyser for CO and CO₂. Proceedings of the Combustion Institute 32, 2051-2058.

Determine Rates of the reduction of Fe_2O_3 to Fe_3O_4 with CO

100Fe

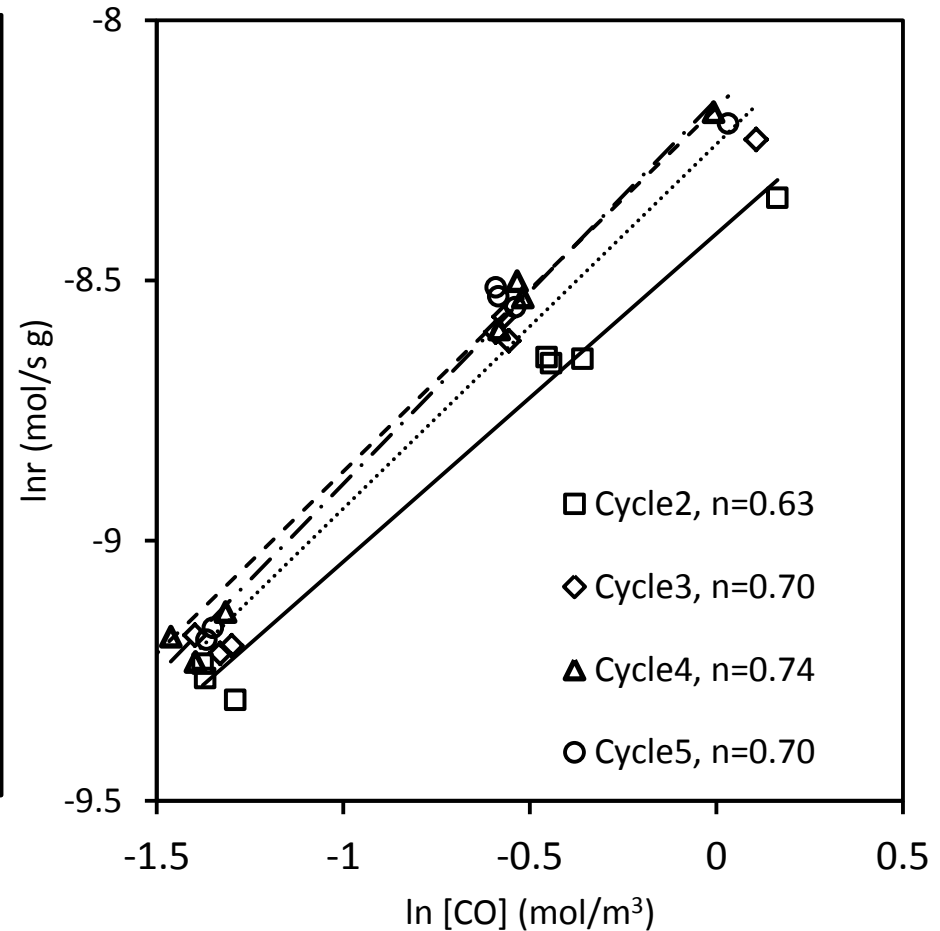
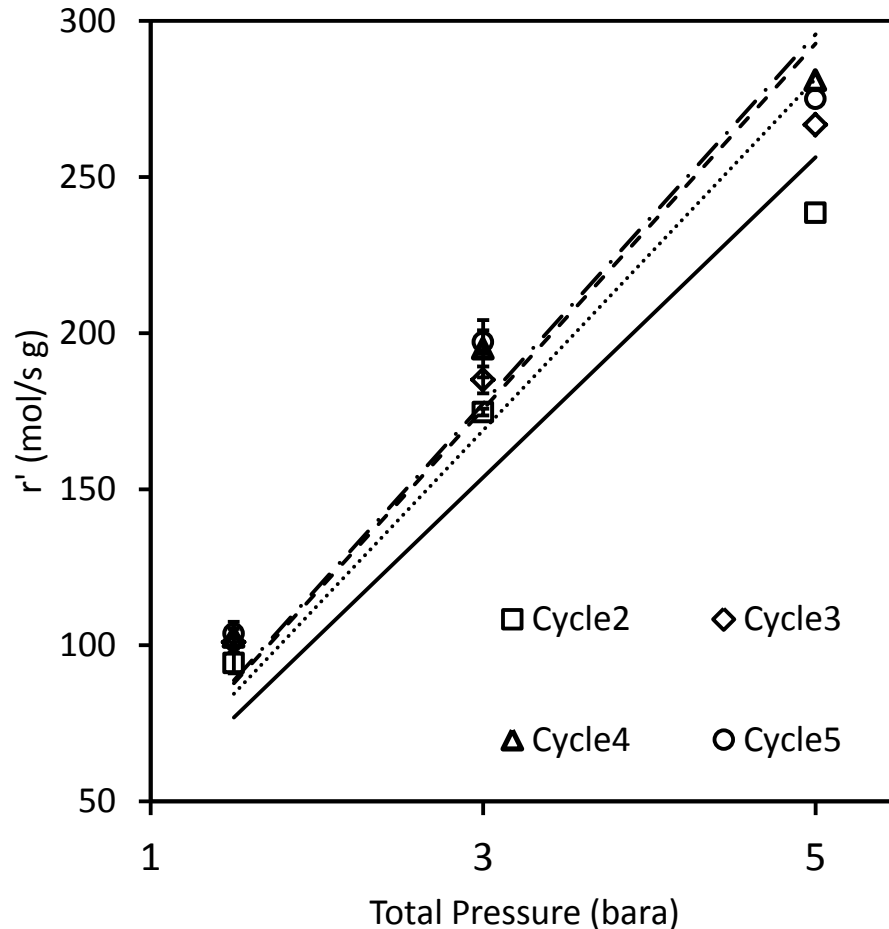


60Fe40Al



Pressurised Experiments

Dependence of the observed rate of reduction on total pressure and concentration of CO (partial pressure)



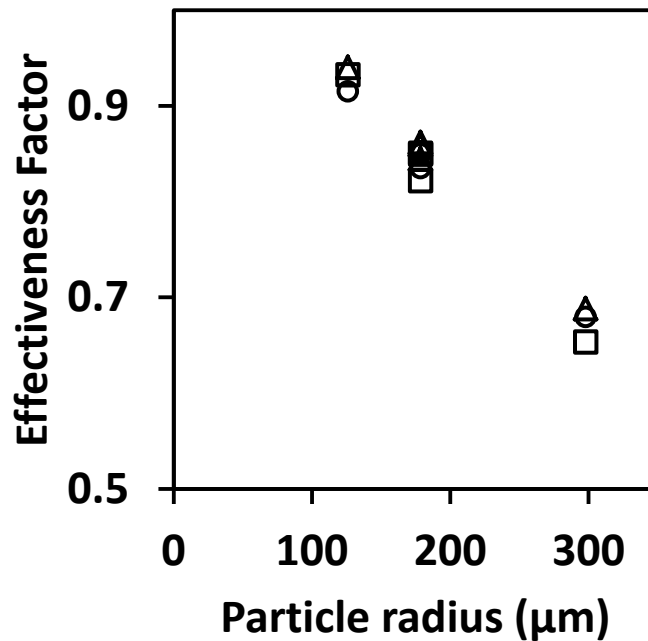
Initial indications, order of reaction slightly lower than 1

Surface Area and Porosimetry Results Summary

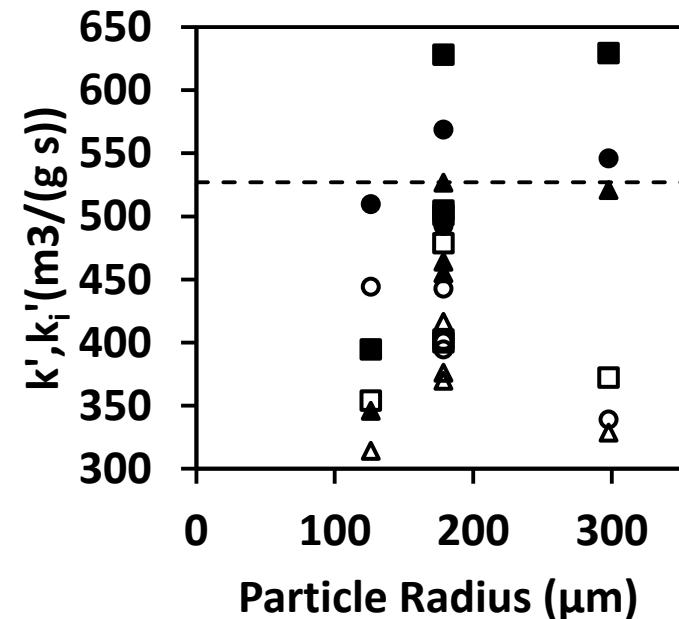
Oxygen Carriers	BET surface area [m ² /g]	Porosity, ϵ (5 nm -10 μ m)
60Fe40Al Fresh	29.0	0.69
60Fe40Al Ox 600°C	28.5	0.68
60Fe40Al Re 600°C	27.6	0.69
60Fe40Al Ox 700°C	26.5	0.69
60Fe40Al Re 700°C	27.8	0.70
60Fe40Al Ox 3bara	30.2	0.69
60Fe40Al Ox 5bara	30.9	0.70

Analysis of intrinsic kinetics of the Fe_2O_3 -based particles

Example of correction for pseudo-intrinsic rate for $^{60}\text{Fe}/^{40}\text{Al}$



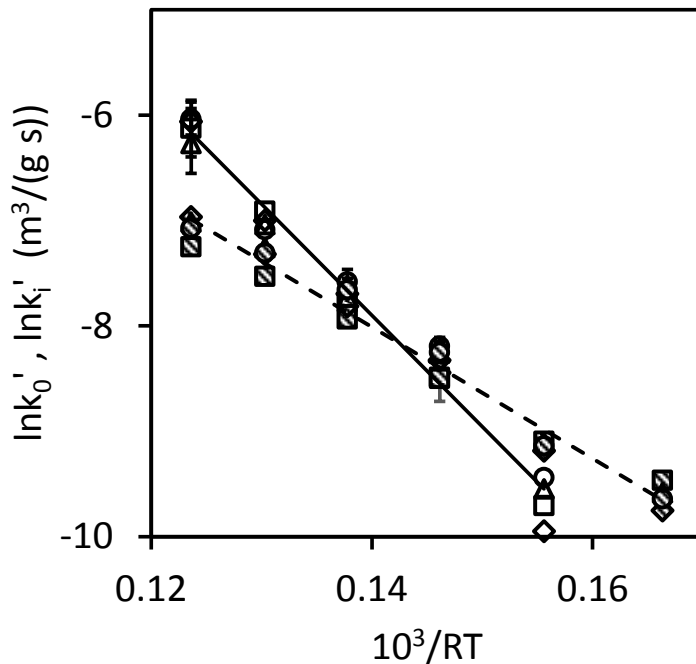
Δ Cycle 3 \circ Cycle 4 \square Cycle 5



Δ k' , cycle 3 \circ k' , cycle 4
 \blacktriangle k_i' , cycle 3 \bullet k_i' , cycle 4
 - - - k_i , average \square k' , cycle 5
 \blacksquare k_i' , cycle 5

Here, used 150 – 212 radius particles. Effectiveness factor a small but important correction.

Activation energy based on pseudo-intrinsic rate constants k_i' for 100Fe and 60Fe40Al



Different slope
(activation energy)
and intercept (pre-
exponential factor)
means **different
surface reaction
mechanism may
involved**

- 60Fe40Al Cycle2
- ◇ 60Fe40Al Cycle3
- △ 60Fe40Al Cycle4
- 60Fe40Al Cycle5
- 100Fe Cycle2
- ◆ 100Fe Cycle3
- ▲ 100Fe Cycle4
- 100Fe Cycle5

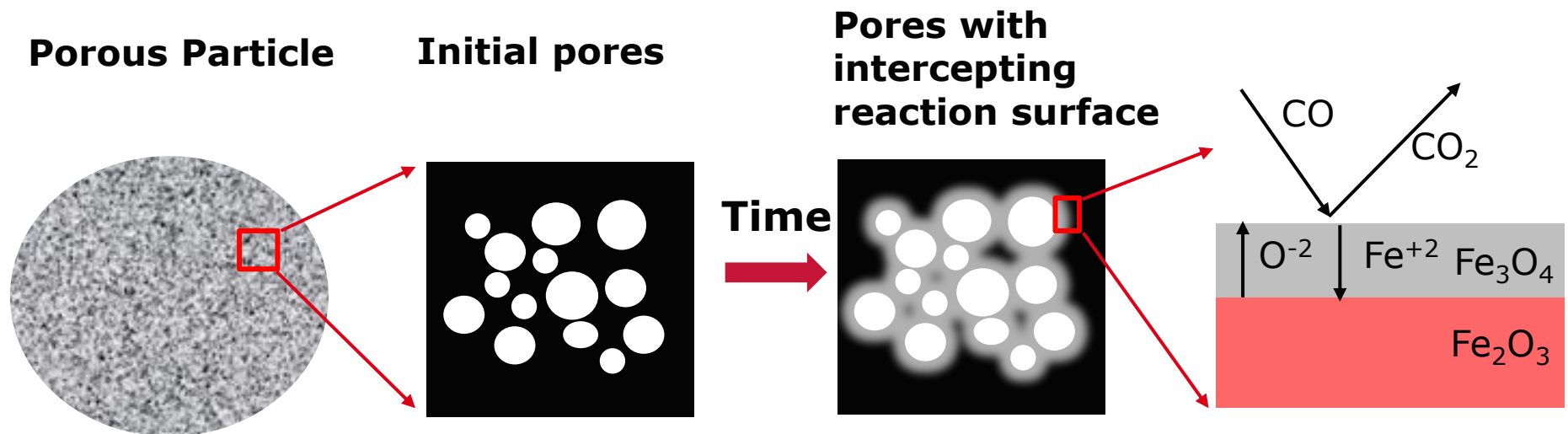
Evaluation of activation energy and pre-exponential factor using student t-statistics at a confidence level of 95%

Oxygen Carriers	Cycle number	Activation Energy, E (KJ/mol)	Ln pre-exponential factor, $\ln A(\text{m s}^{-1})$
60Fe40Al	Cycle2	110±12	7.5±0.1
	Cycle3	115±11	8.2±0.1
	Cycle4	97±13.0	5.7±0.1
	Cycle5	101±14	6.3±0.1
100Fe	Cycle2	61±9	0.3±0.1
	Cycle3	64±8	0.9±0.1
	Cycle4	65±9	1.1±0.1
	Cycle5	63±10	0.9±0.1

Detailed reaction model for the reduction of iron-based oxygen carrier

Random pore model

- The pseudo-intrinsic kinetics showed that the gas phase effectiveness factor is high for both particles, so **no concentration gradient across particle**
- The random pore model treats a solid particle as assembly of randomly oriented cylindrical pores isolated by solid phase.
- It assumes:
Pore size, number of pores, total pore length are constant.



Use of random pore model for the reduction of Fe_2O_3 -based oxygen carrier

Initial surface reaction
rate constant

$$k' = \frac{k'_{s,0} c_{\text{CO},s} S_0 (1 - X) \sqrt{1 - \psi \ln(1 - X)}}{(1 - \varepsilon_0) (M_{\text{Fe}_2\text{O}_3} c_{\text{CO},b}) \left(1 + \frac{\beta \alpha}{\psi} (\sqrt{1 - \psi \ln(1 - X)} - 1)\right)}$$

Structure parameter: $\psi = \frac{4\pi L_0 (1 - \varepsilon_0)}{S_0}$

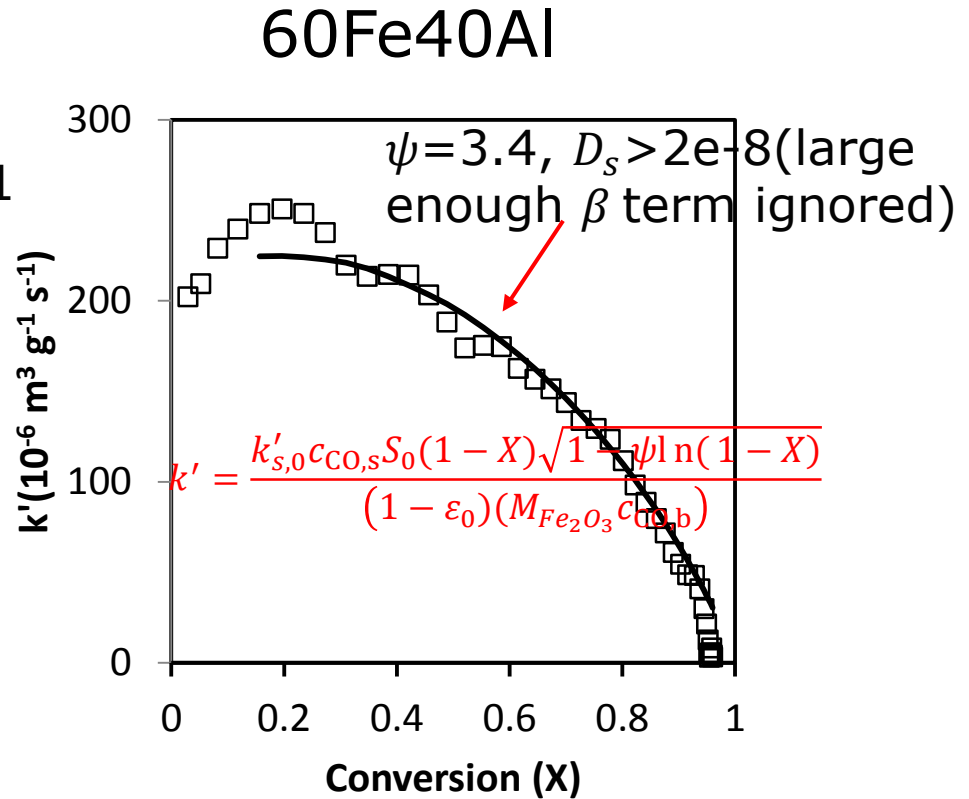
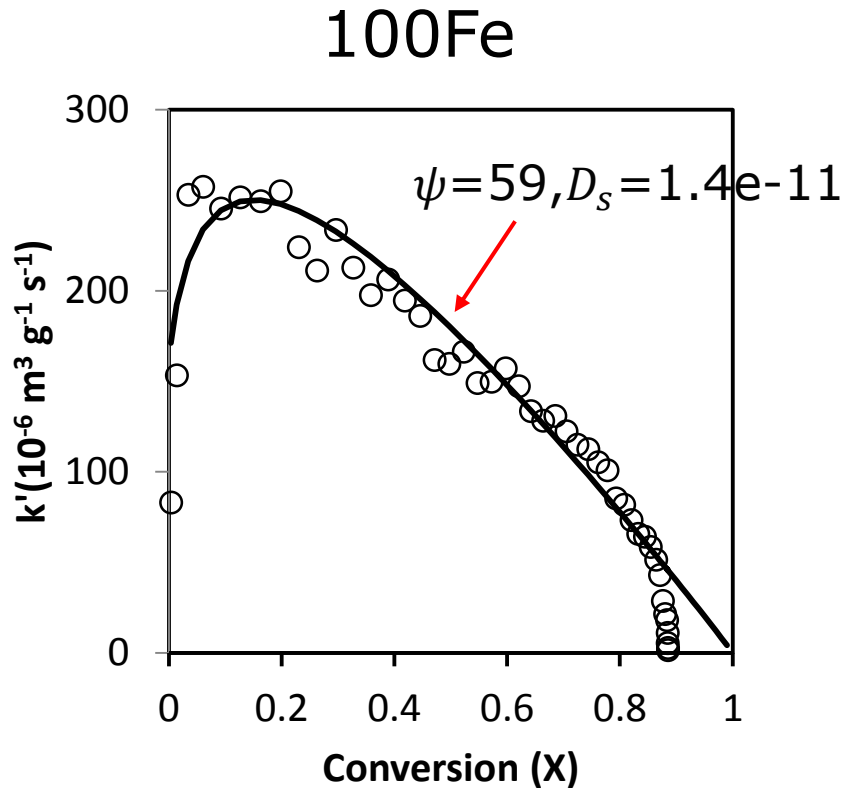
$L_0 = \frac{1}{\pi} \int_0^\infty \frac{v_{\text{pore}}}{r_{\text{pore}}^2} dr_{\text{pore}}$

Specific length of pore

Modified Biot number: $\beta = \frac{2k'_{s,0} (1 - \varepsilon_0)}{V_{\text{Fe}_2\text{O}_3} S_0 D_s}$

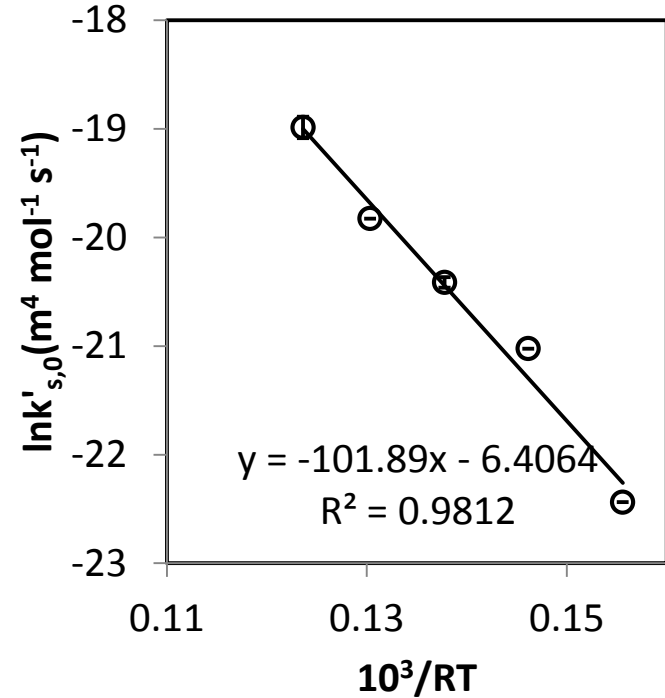
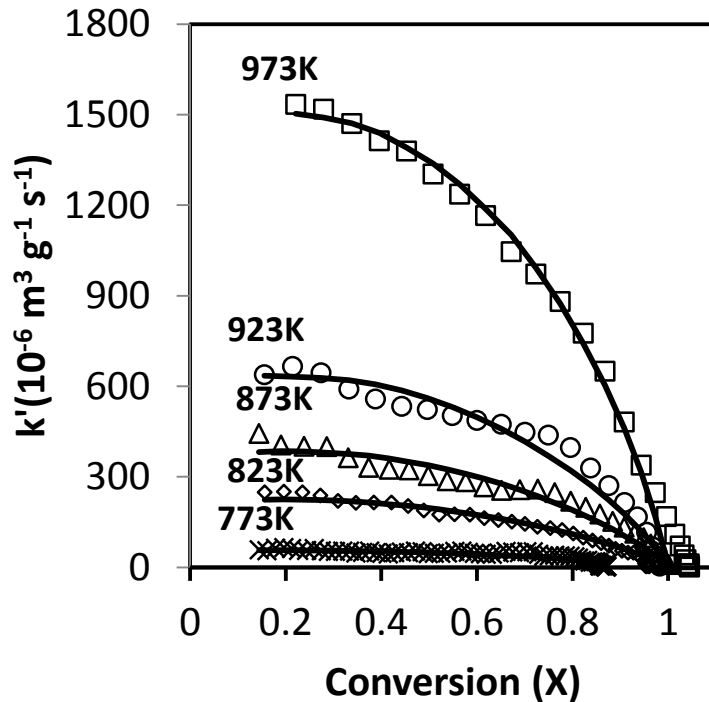
Ionic diffusivity

Difference in surface reaction mechanism deduced from random pore model



The curve was fitted using Trust-Region-Reflective Least Squares algorithm in matlab

Intrinsic surface reaction constant at different temperatures derived from random pore model

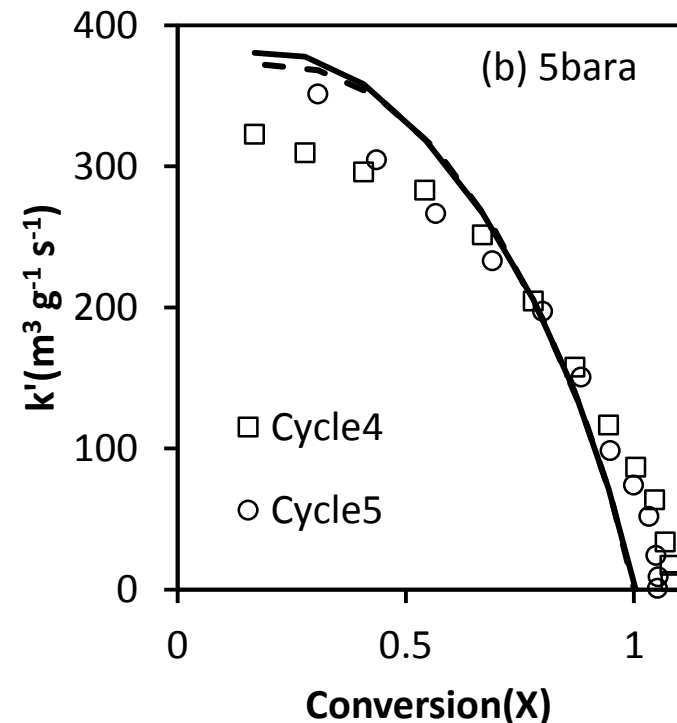
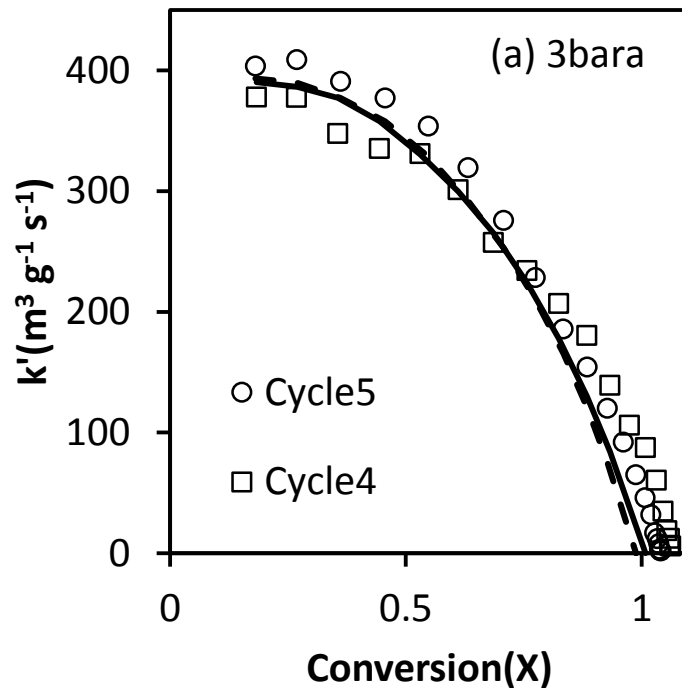


Intrinsic surface reaction constant:

Similar to the E obtained in earlier intrinsic analysis

$$k'_{s,0} = 1.8 \times 10^{-3} \exp\left(\frac{-102 \text{ kJ mol}^{-1}}{RT}\right) \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$$

Random pore model for supported iron oxide at elevated pressure



The $k'_{s,0}$ obtained using equation in previous slides was used for fitting the random pore model at elevated pressure.

The reactor model used to validate the assumptions used in intrinsic rate derivation.

For inlet mixing:

$$\tau_1 \frac{dY}{dt} = Y_{-1} - Y_0$$

For each element in Bubble Phase:

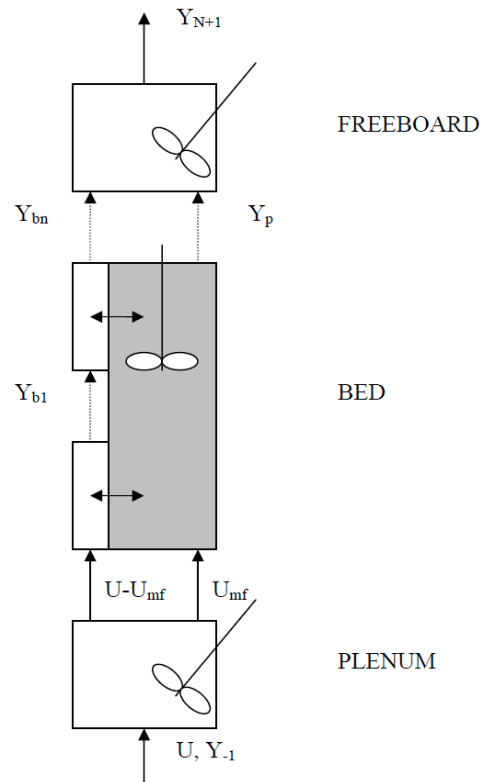
$$\frac{dY_b}{dt} = \frac{-(U - U_{mf})}{\varepsilon_b} \frac{\partial y}{\partial z} + \frac{Q}{V_b} (Y_p - Y_b)$$

For the whole particulate Phase:

$$\frac{dY_p}{dt} = \frac{-U_{mf}}{\varepsilon_{mf}(1 - \varepsilon_b)} \frac{\Delta Y_p}{H} - \frac{Q \varepsilon_b}{\varepsilon_{mf}(1 - \varepsilon_b)} \sum \frac{Q \varepsilon_b}{V_b} (Y_p - Y_b) \frac{\Delta z}{H} + \frac{R}{\rho_m \varepsilon_{mf}}$$

For free board and subsequent mixing:

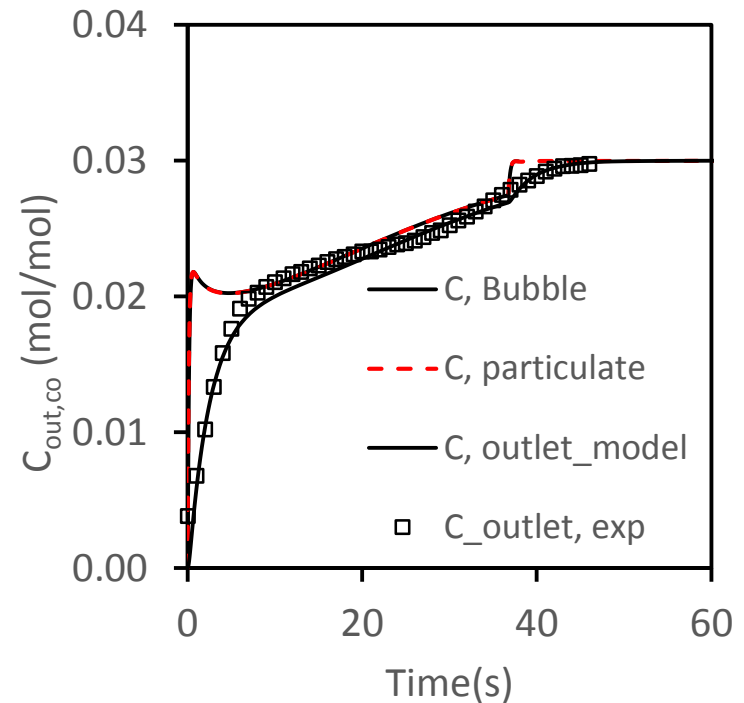
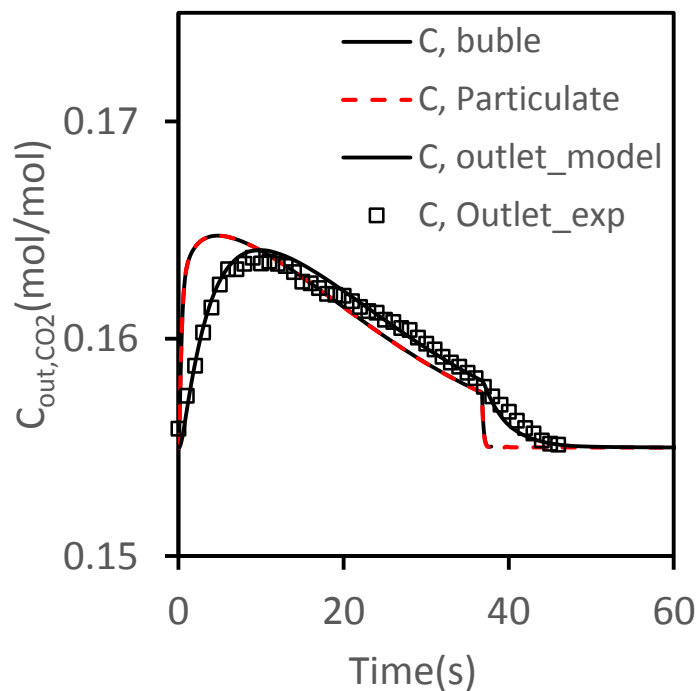
$$\tau_2 \frac{dY_{N+1}}{dt} = Y_{pN} \left(\frac{U_{mf}}{U} \right) + Y_{bN} \left(\frac{U - U_{mf}}{U} \right) - Y_{N+1}$$



An example of Input parameters for the reactor model

Input Parameters	Value
Reactor inside diameter, D_c (m)	0.029
Cross sectional area of the bed, A_r (m ²)	6.6×10^{-4}
Temperature of the bed, T (K)	823
Minimum fluidizing velocity, U_{mf} (m s ⁻¹)	0.147
Voidage at minimum fluidization, ϵ_{mf}	0.4
No. of volume	100
Pressure, P (Pa)	1.01×10^5
Height of the bed at minimum fluidisation, H_{mf}	0.065
Derived Parameters	Value
Fluidizing velocity, U (m s ⁻¹)	$2.5 \cdot P \cdot U_{mf}$
Mean bubble diameter, d_b (m)	$0.54 \cdot (P \cdot U - P \cdot U_{mf})^{0.4} \cdot P \cdot H^{0.8/1.8} / 9.81^{0.2}$
Bubble rising velocity based on mean bubble diameter, U_b (m s ⁻¹)	$P \cdot U - P \cdot U_{mf} + 0.71 \cdot (9.81 \cdot P \cdot D_b)^{0.5}$
Bubble volume (m ³)	$P \cdot V_b = \pi \cdot P \cdot D_b^3 / 6$
Height of the bed when fluidising, H (m)	$(H - P \cdot H_{mf})^{0.3894} \cdot 9.81^{0.4} \cdot H^{0.4} / (P \cdot U - P \cdot U_{mf})^{0.8} - P \cdot H_{mf}$
Cross flow rate, Q (m ³ s ⁻¹)	$\pi \cdot P \cdot D_b^2 / 4 \cdot P \cdot U_{mf} \cdot 3$
Bubble fraction, ϵ_b	$1 - P \cdot H_{mf} / P \cdot H$

Validation of the reaction model by incorporating it into a complete fluidized bed model



By feeding the random pore model into a complete reactor model assuming complete mixing in particulate phase, the overall numerical model satisfactorily predict the outlet concentration of CO and CO₂

Conclusions

- Two iron-based oxygen carriers, a supported iron oxide (60Fe40Al₂) and an unsupported iron oxide (100Fe) were prepared by a simple wet granulation method.
- A 3kw fluidised bed reactor was used to investigate the intrinsic kinetics of the reduction of those Fe-based iron oxide at high temperature and elevated pressure.
- The pseudo-intrinsic rate constants and activation energies for the supported iron oxide (60Fe40Al) and unsupported iron oxide (100Fe) have been derived.
- Difference in the activation energy and pre-exponential factor between 60Fe40Al and 100Fe is observed, suggesting a different surface reaction mechanism may involved.
- A more detailed reaction model, i.e., a random pore model, was proved to satisfactorily apply to both types of particles. A difference in $D_{s,0}$ was noted, which was large enough for 60Fe40Al suggest surface adsorption may be in control.

Conclusions

- Pressurised experiments with 60Fe40Al shows the observed reactions order of the reduction with CO to Fe_3O_4 is slightly lower than 1.
- Intrinsic reaction model developed for atmospheric pressure was shown to be suitable to predict the reaction kinetics at elevated pressure, the deviation at 5 bara was likely to be a result of decrease in effectiveness factor at higher pressure.
- The reaction model developed using reasonable assumptions were validated by plug the model into a two-phase reactor model. The model outlet concentration was shown to agree with that was observed.

Acknowledgements

We gratefully acknowledge funding from the EPSRC under grants

EP/I010912/1: Multi-scale evaluation of advanced technologies for capturing the CO₂: chemical looping applied to solid fuels.

EP/K000446/1: UKCCSRC - The United Kingdom Carbon Capture and Storage Research Centre

And UKCCSRC-C1-39: Chemical looping for low-cost oxygen production and other applications

The Energy Programme is a Research Councils UK cross council initiative led by EPSRC and contributed to by ESRC, NERC, BBSRC and STFC

EPSRC

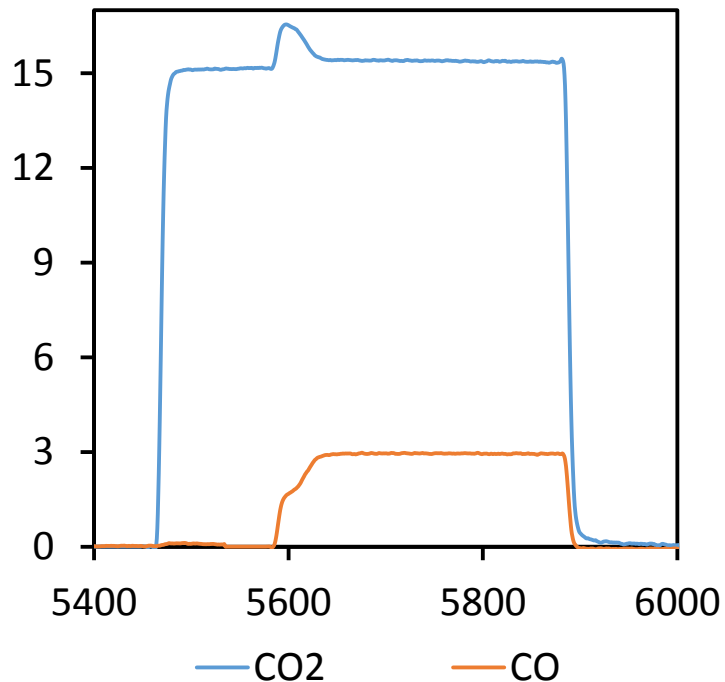
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Thank you!

Q&A

Details of 4th cycle of 60Fe40Al reduction with CO in the presence of H₂S at 823 K, 1 bar



Procedure:

Reduction Cycle:

N₂ purge 120s

N₂+CO₂ 120s

N₂+CO₂+CO 300s

Oxidation cycle:

N₂ purge 120s

N₂+Air 300s

Estimation of Intrinsic rate constant and effectiveness factor

From a pseudo-steady state assumption, the rate of CO entering a surface of spherical particles must be equal to the rate of the chemical reaction with in the particle, then for a first order irreversible reaction in a porous particle:

$$\begin{aligned} r' &= k' c_{\text{CO},P} \\ \frac{1}{k'} &= \frac{R \rho_{\text{Fe}_2\text{O}_3}}{3 k_{g,\text{CO}}} + \frac{1}{\eta_{\text{CO}} k'_i} \end{aligned} \quad (1)$$

Also for a porous spherical particle, a mass balance of CO within a spherical shell of the particle gives:

$$\begin{aligned} \eta_{\text{CO}} &= \frac{3}{\phi^2} (\phi \coth \phi - 1) \\ \phi &= \sqrt{\frac{k'_i \rho_{\text{Fe}_2\text{O}_3}}{D_{e,\text{CO}}}} R \end{aligned} \quad (2)$$

k'_i and η_{CO} could be solved iteratively by converging the effectiveness factor in equation (1) and equation (2) with an initial input of $\eta_{\text{CO}} = 1$. $k_{g,\text{CO}}$ and $D_{e,\text{CO}}$ need to be estimated first before the iteration.

Calculating Effective diffusivity

The effective diffusivity, D_e , in equation (2) was estimated from the bulk diffusivity, D_b (obtained from Chapman-Enskog kinetic theory)^[1] and Knudsen diffusivity, D_K ^[2] with experimental data, and used τ as a fitted tortuosity factor, which takes in account the effect of the tortuous path within the particle on the effective diffusivity

$$\frac{1}{D_e} = \frac{\epsilon_{\text{Fe}_2\text{O}_3}}{\tau} \left(\frac{1}{D_K} + \frac{1}{D_b} \right) \quad (3)$$

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

$$D_K = 97 r_e \sqrt{\frac{T}{M}} = 194 \frac{\epsilon_{\text{Fe}_2\text{O}_3}}{S_g \rho_{\text{Fe}_2\text{O}_3}} \sqrt{\frac{T}{M}} \quad (5)$$

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

[2] SATTERFIELD, C. N. 1980a. *Heterogeneous catalysis in practice*, New York ; London, McGraw-Hill.

Calculating external mass transfer coefficient

The external mass transfer coefficient, k_g , in equation (1) was calculated using the definition of Sherwood number, and Sherwood number was estimated using a correlation ^[3]. The velocity of the gas, U , was calculated using an inlet flow rate of 50 ml/min (293K) and height of the pan of 11mm:

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

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

Where

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

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

Procedure for deriving intrinsic rate constant and activation energy

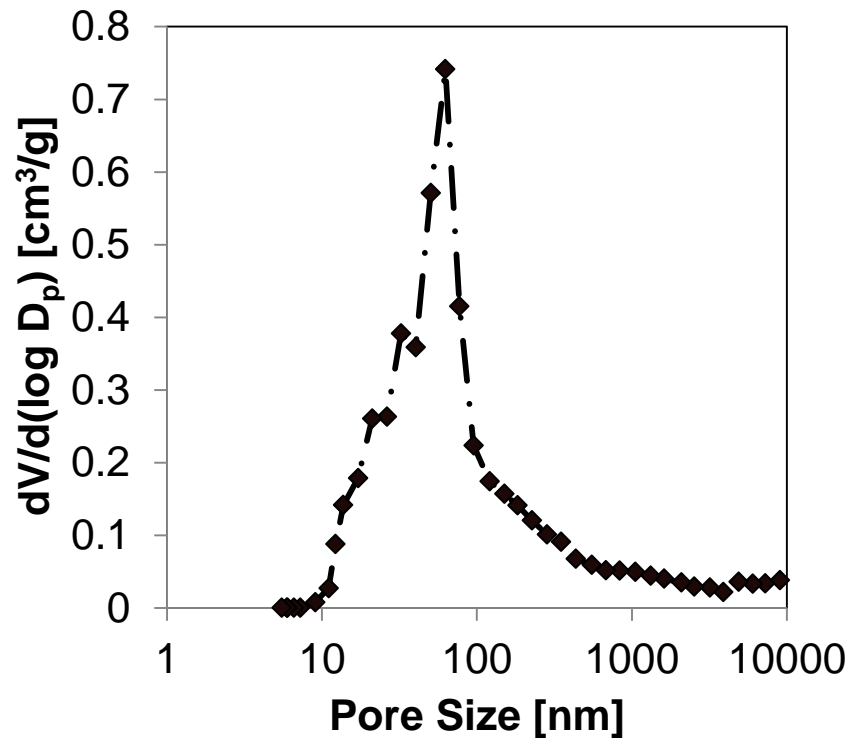
Step 1: Calculate k_g . Calculate D_e assuming $\tau=4$

Step 2: Calculate k'_i and η_{co} in equation (1)
(First loop assuming $\eta_{co}=1$)

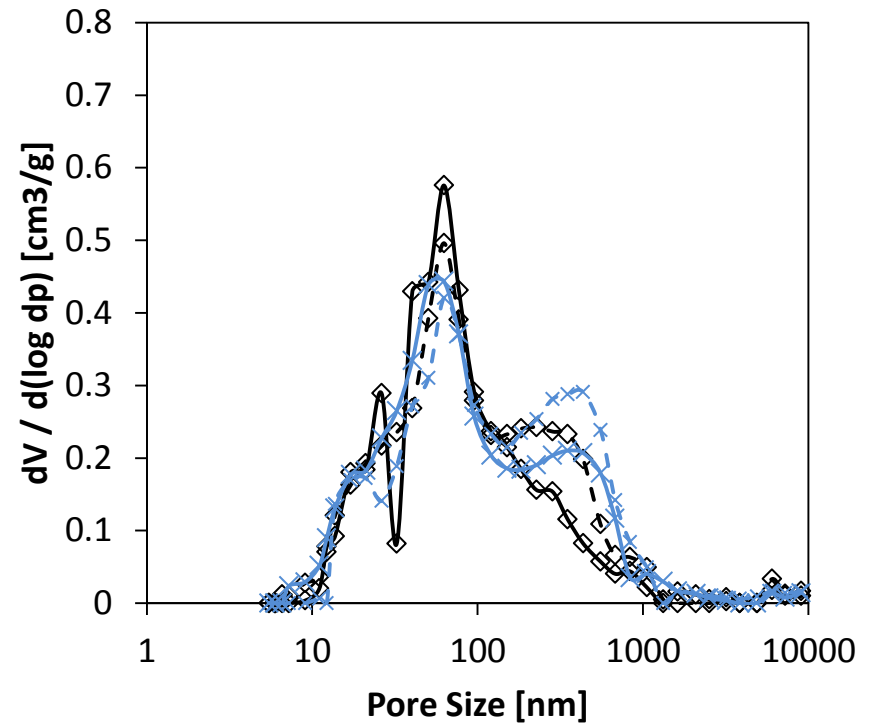
Step 3: Using the k'_i and D_e Calculated earlier to estimate a new value of η_{co} in equation (2)

Step 4: Calculate k'_i and η_{co} in equation (1)
using the new value of η_{co}

Step 5: Repeat step 2 to step 4 until η_{co} converge



◆ $\cdot 60\text{Fe}40\text{Al}2$

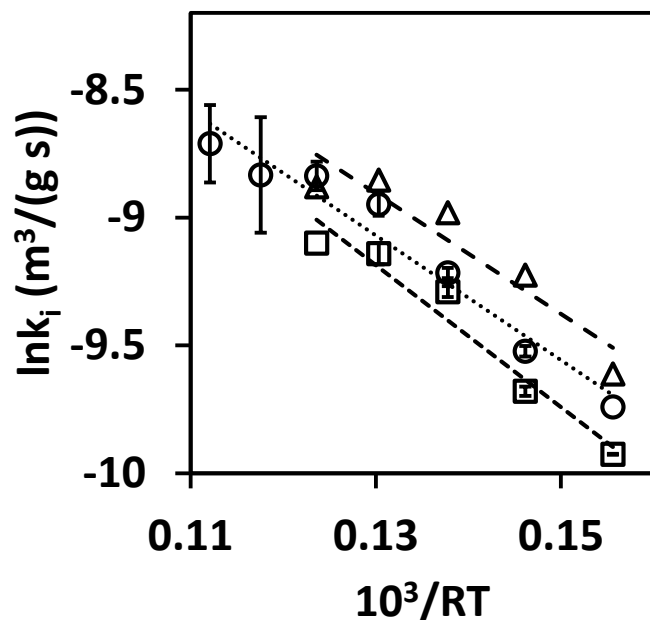


◆ 600C, Ox ◆ 600C, Red
 × 700C, Ox × 700C, Red

As the reaction proceeds, some pores are shifted from approx. 70 nm to 200 nm, improving pore interconnection – reactivity increases slightly.

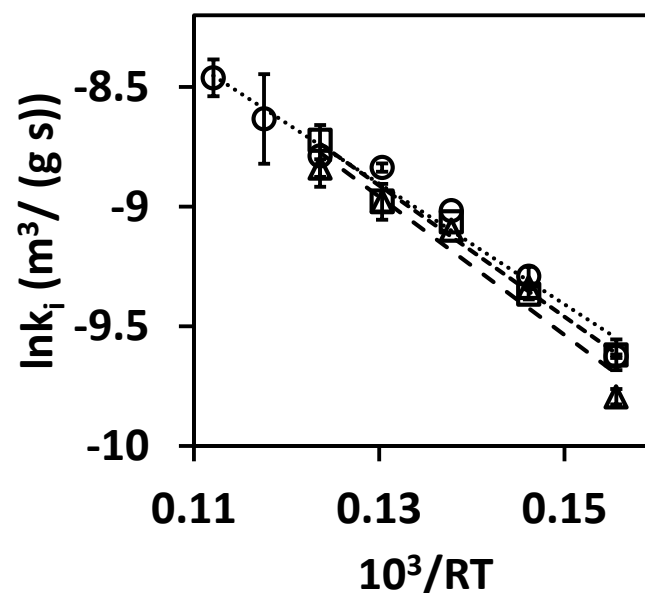
Dependence on Temperature-Activation Energy

100%Fe



○ S method △ E method □ B method

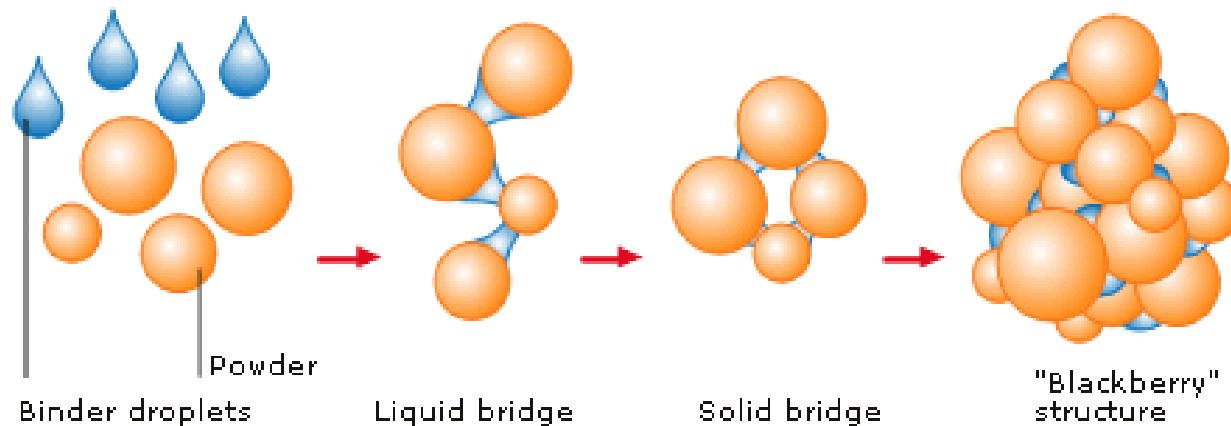
60%Fe40%Al



○ S Method △ E Method □ B Method

Activation energy and pre-exponential factor was found via TGA results of ~2mg samples at a fixed CO concentration of 3vol% under varying temperature from 500°C – 800°C.

Wet granulation From Fe_2O_3 and different Al_2O_3 precursors:



The 60 wt.% Fe_2O_3 / 40 wt.% Al_2O_3 (60Fe40Al) particles were prepared via a simple wet granulation technique from Fe_2O_3 powder (5 μm Sigma Aldrich) and four different types of Al_2O_3 precursor powders:

- 1.60Fe40Al1 – Al_2O_3 (10 μm powder, Sigma Aldrich)
- 2.60Fe40Al2 – $\text{Al}(\text{OH})_3$ (Sigma Aldrich)
- 3.60Fe40Al3 – $\text{Al}(\text{OH})\text{O}$ (Sasol Pural NF, $d_{50} = 15 \mu\text{m}$)
- 4.60Fe40Al4 – $\text{Al}(\text{OH})\text{O}$ (Sasol Pural SCF 55, 83% < 25 μm)