SOME RESEARCH ON CLEAN COAL TECHNOLOGY

CO_2 SEPARATION AND CAPTURE

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OUR APPROACHES FOR CO_2 CAPTURE

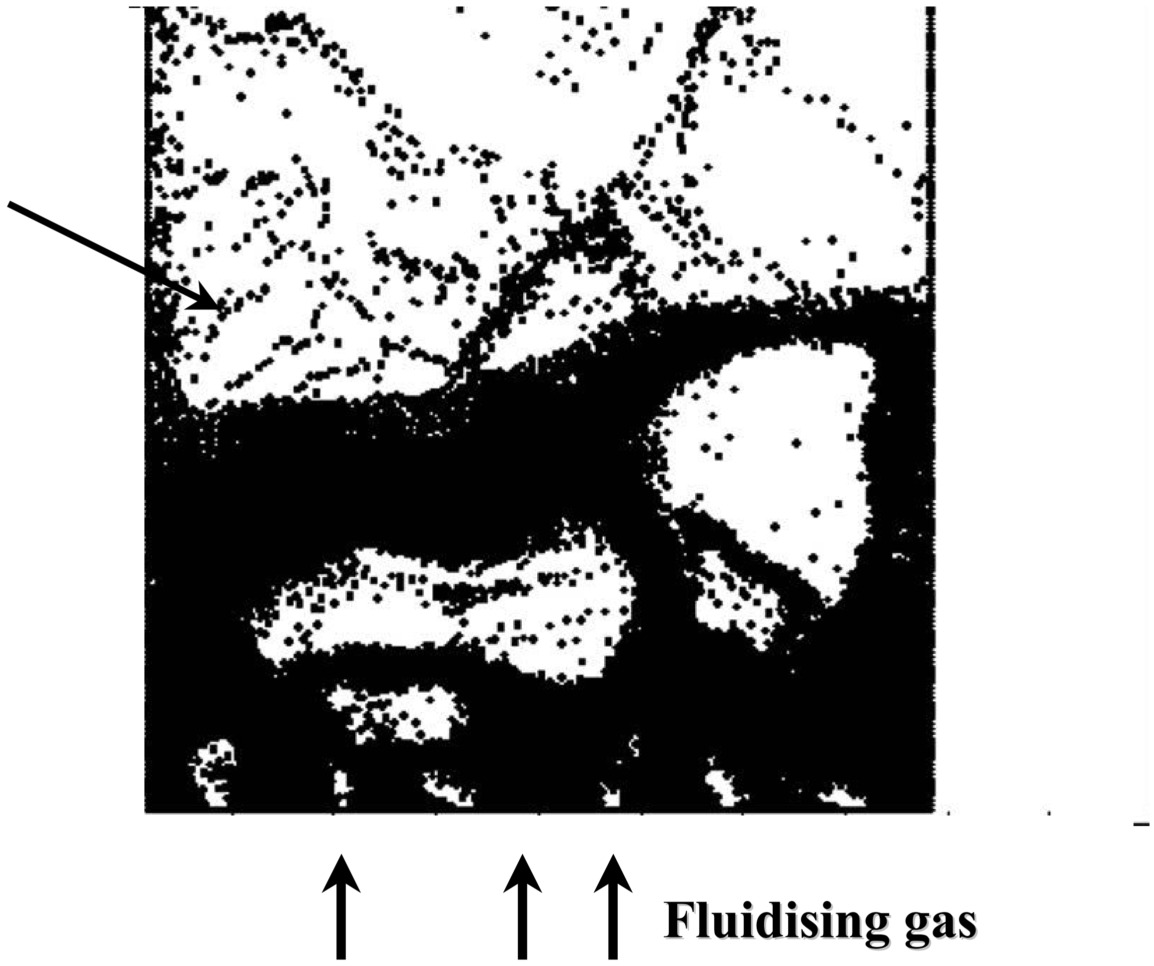
Focus on longer-term techniques which could have higher cycle efficiency than retro-fitted pulverised fuel furnaces

Fluidised Bed approaches with:

- **Oxy-fuel**
  Separate oxygen from air before combustion
  Combust coal in O_2/CO_2 - separation is mainly water / CO_2
- **Gasification and pre-combustion CO_2 separation**
  Capture CO_2 under reducing conditions pre-combustion.
- **Chemical Looping**
  Uses solid oxygen carrier.

High pressure possible ⇒ combined cycle

FLUIDISED BED



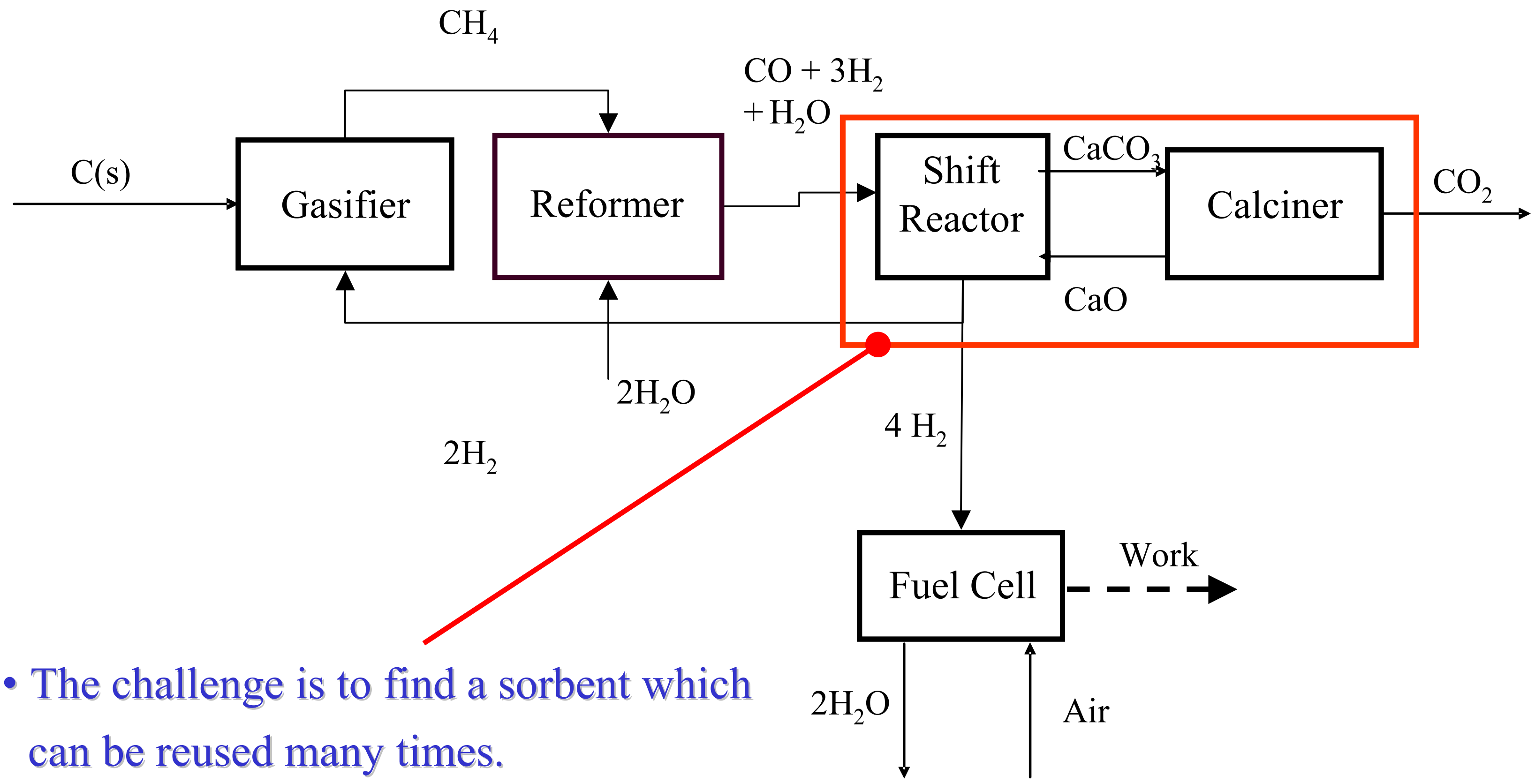
Granular particles, *e.g.* sand, coal ash…

Fluidising gas

- **small footprint/MW**
- **robust to fuel changes**
- ***in situ* capture of *e.g.* SO_x**
- **<u>pressurised operation</u>**

Example 1 – Gasification

ZECA – Generation of H_2 from coal and pure CO_2 for sequestration



- The challenge is to find a sorbent which can be reused many times.
- Natural limestone (mainly $CaCO_3$) degrades. How can it be improved, based on a fundamental understanding of the reactions involved? Synthetic sorbents?

KEY REACTIONS

$C + 2H_2 \rightarrow CH_4$ *Hydrogasification*

$CH_4 + H_2O \rightarrow CO + 3H_2$ *Reforming*

$CO + H_2O \rightleftharpoons CO_2 + H_2$ *Watergas Shift*

$CO_2 + CaO \rightarrow CaCO_3{}^*$ *Carbonation*

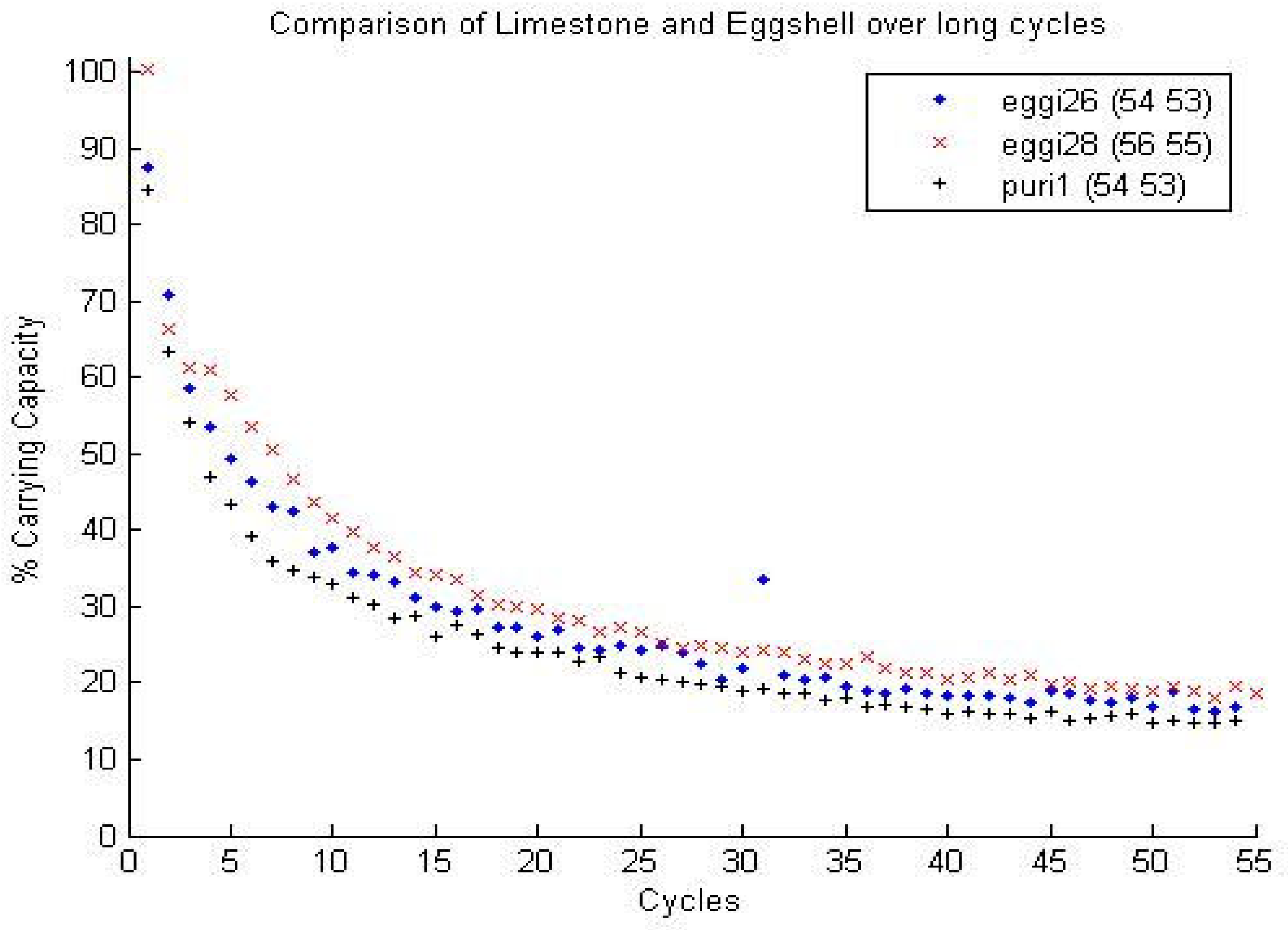
$CaCO_3 \rightarrow CaO + CO_2$ *Calcination*

Separation of H_2 and CO_2

Regeneration of sorbent: CO_2 to storage

* The percentage completion of this reaction (molar basis) is the *carrying capacity* of the solid sorbent.

CARRYING CAPACITY OF NATURAL SORBENTS
Limestone *vs.* Eggshell

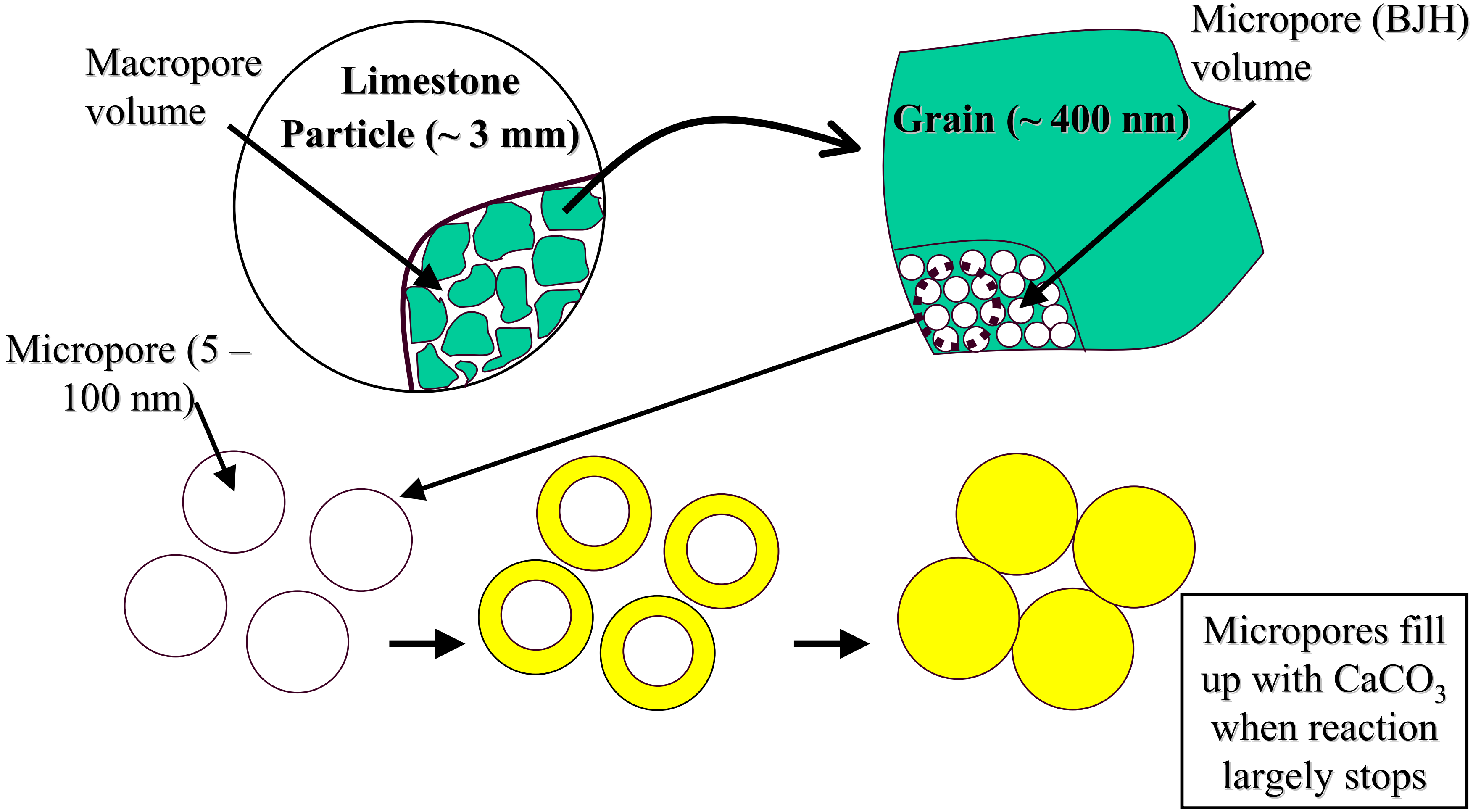


Extended cycles of calcination and carbonation

Uptake of CO_2 confirmed by XRD analysis of carbonated material.

Surprising similarities for disparate materials!

SIMPLE MODEL: REACTION IN PARTICLE



Macropore volume

Limestone Particle (~ 3 mm)

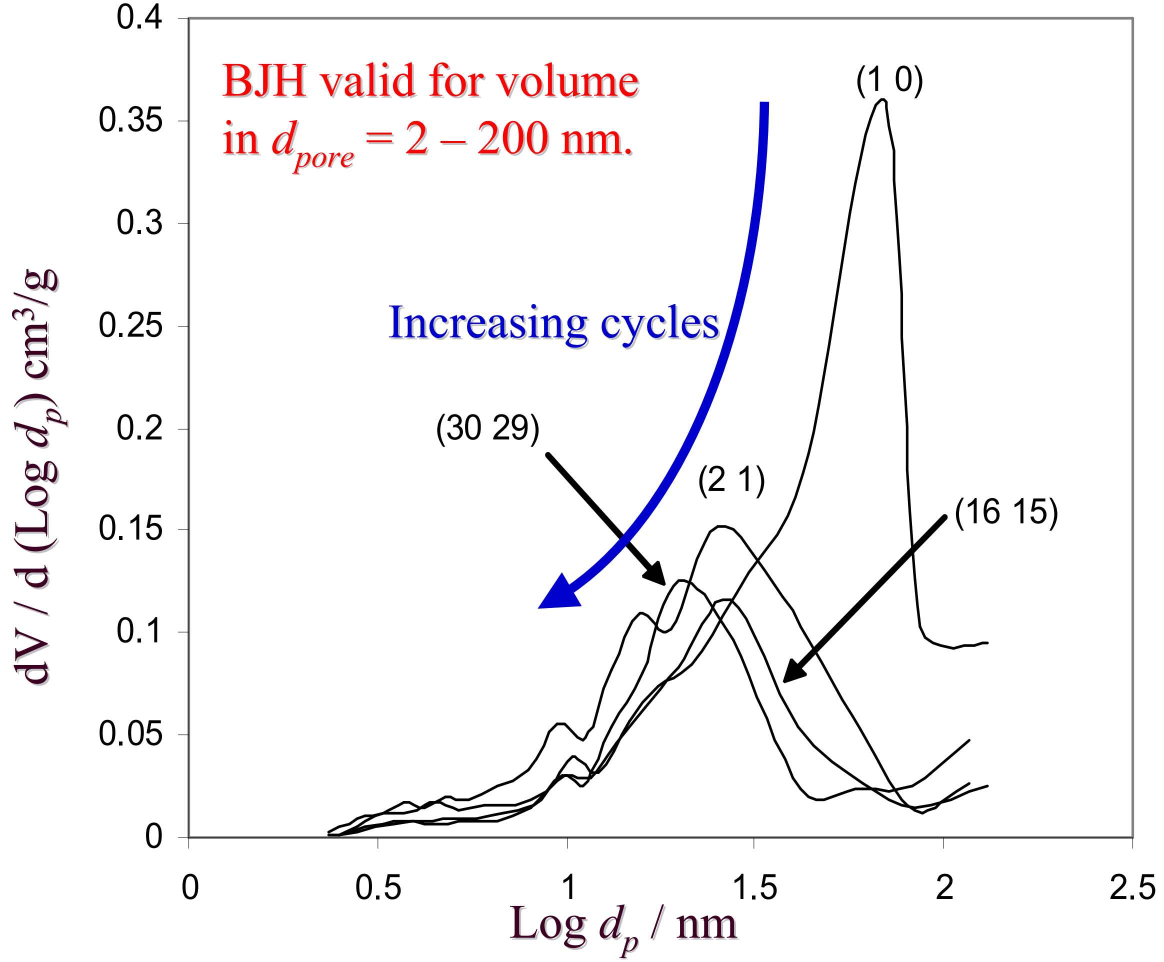
Grain (~ 400 nm)

Micropore (BJH) volume

Micropore (5 – 100 nm)

Micropores fill up with $CaCO_3$ when reaction largely stops

BJH PORE SIZE DISTRIBUTION (Limestone)



BJH valid for volume in $d_{pore} = 2 - 200$ nm.

Closer examination of pores below 100 nm

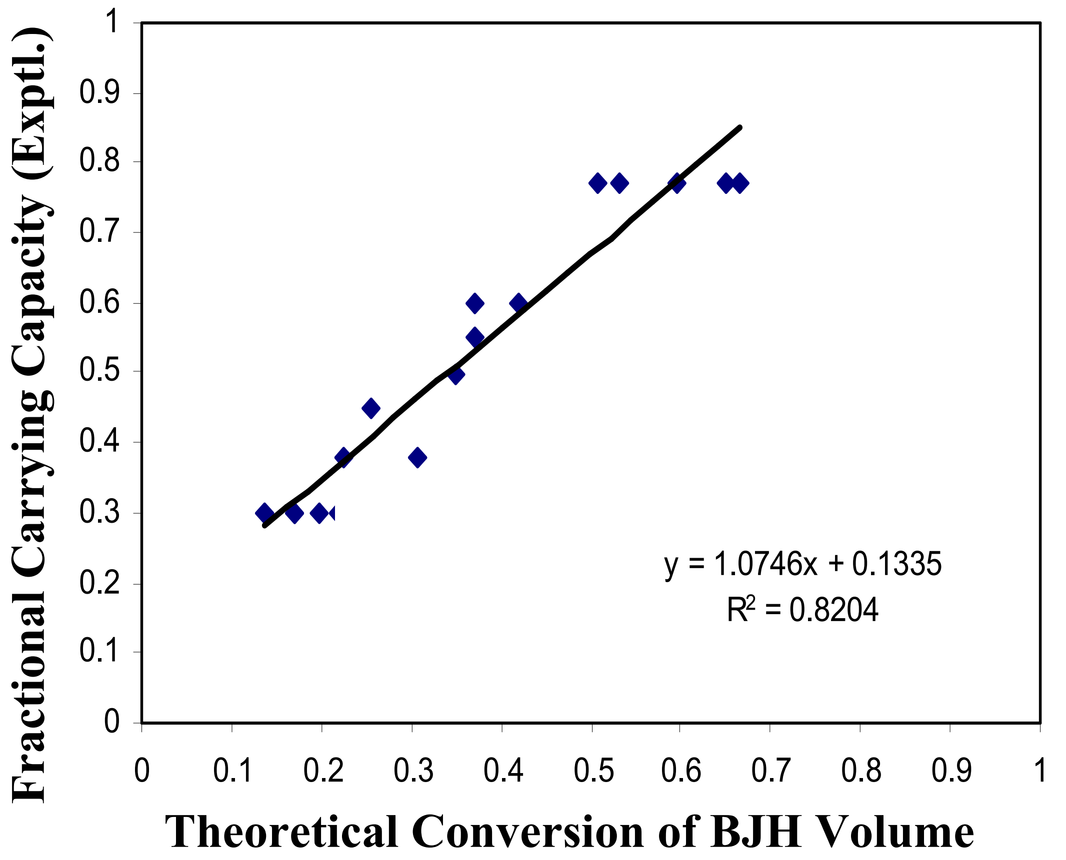
Same trends in other materials:

chalk

eggshell

dolomite.

FRACTIONAL CARRYING CAPACITY



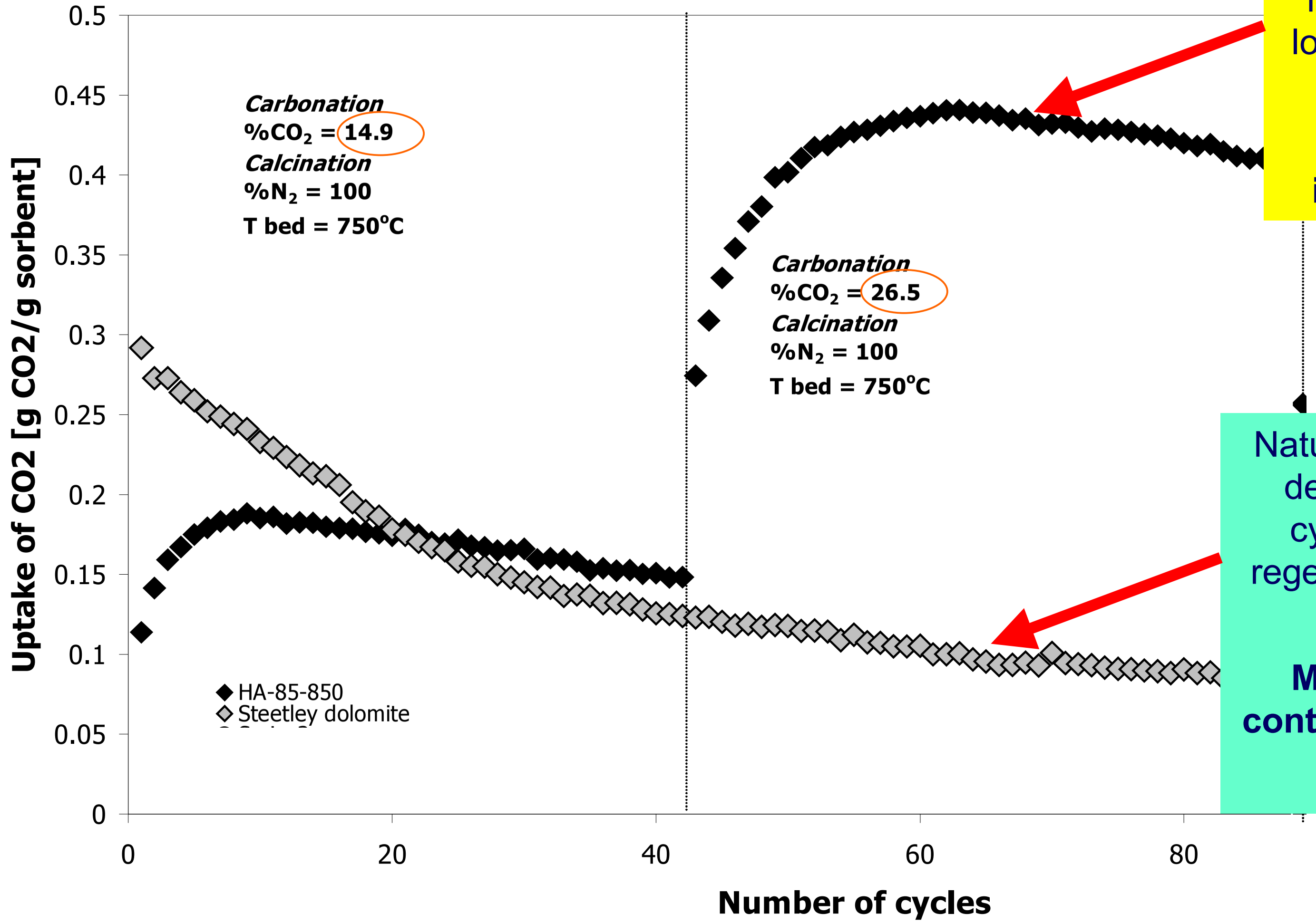
For range of limestones: Purbeck, Cadomin, Penrith, Glen Morrison, Havelock.
Best fit regression line fitted.

Typical residual constant conversion of ~13% is typical of limestone.

Conclusion holds for other materials – chalk, eggshell, etc. These have *much* different/larger macropore volumes than limestone but *comparable* micropore volumes.

BUT they have similar capacity and decay of capacity with cycle.

NEW SYNTHETIC SORBENTS



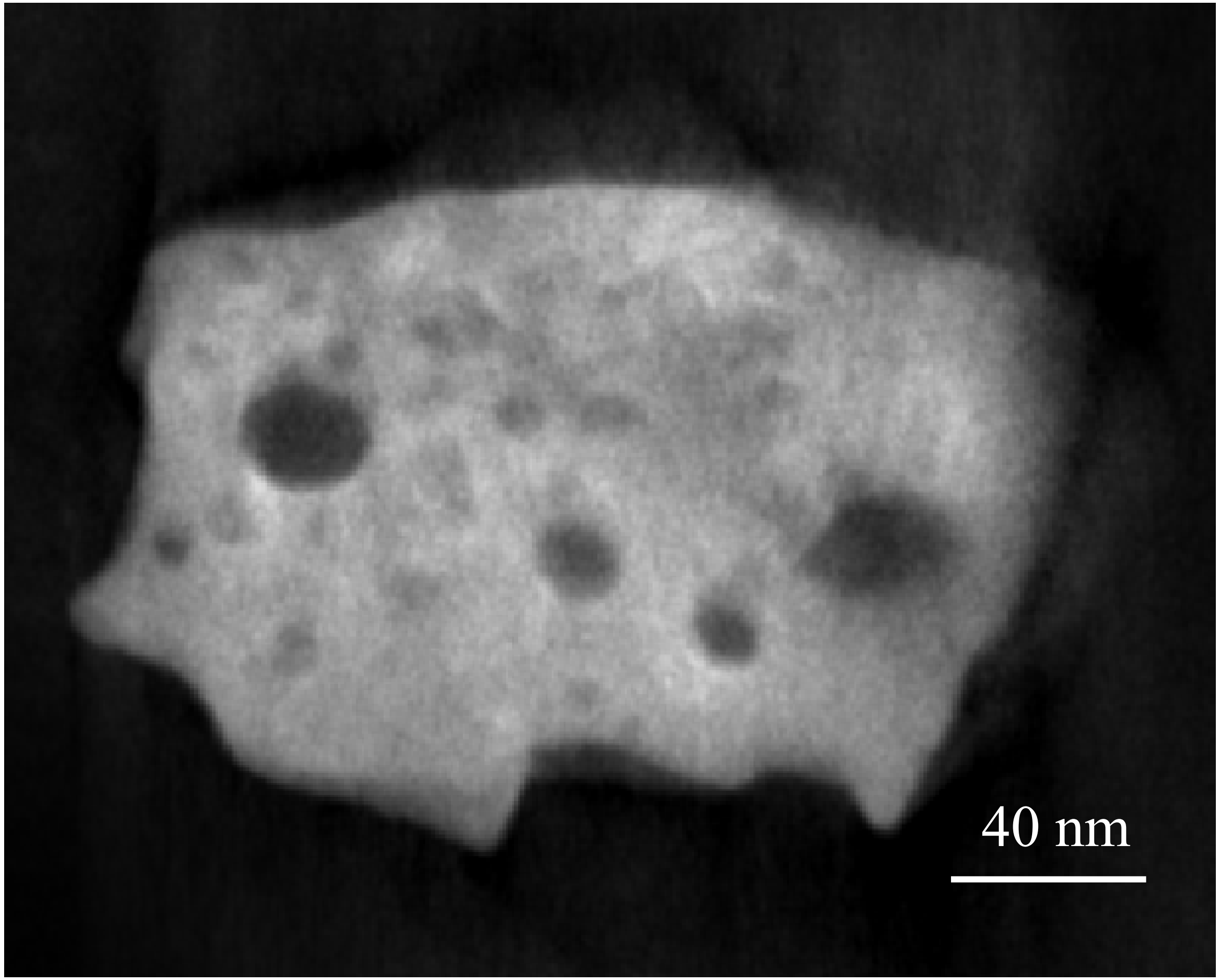
New sorbent - capacity loss much less. Capacity ***increases*** with [CO$_2$]

Micropore volume increases with [CO2]

Natural sorbent - uptake degrades with no. of cycles of sorption & regeneration. Insensitive to [CO$_2$]

Micropore volume continuously decreases

STEM HAADF TOMOGRAPHY - Nanoengineering



Collaboration with Prof. Paul Midgeley, Materials Science

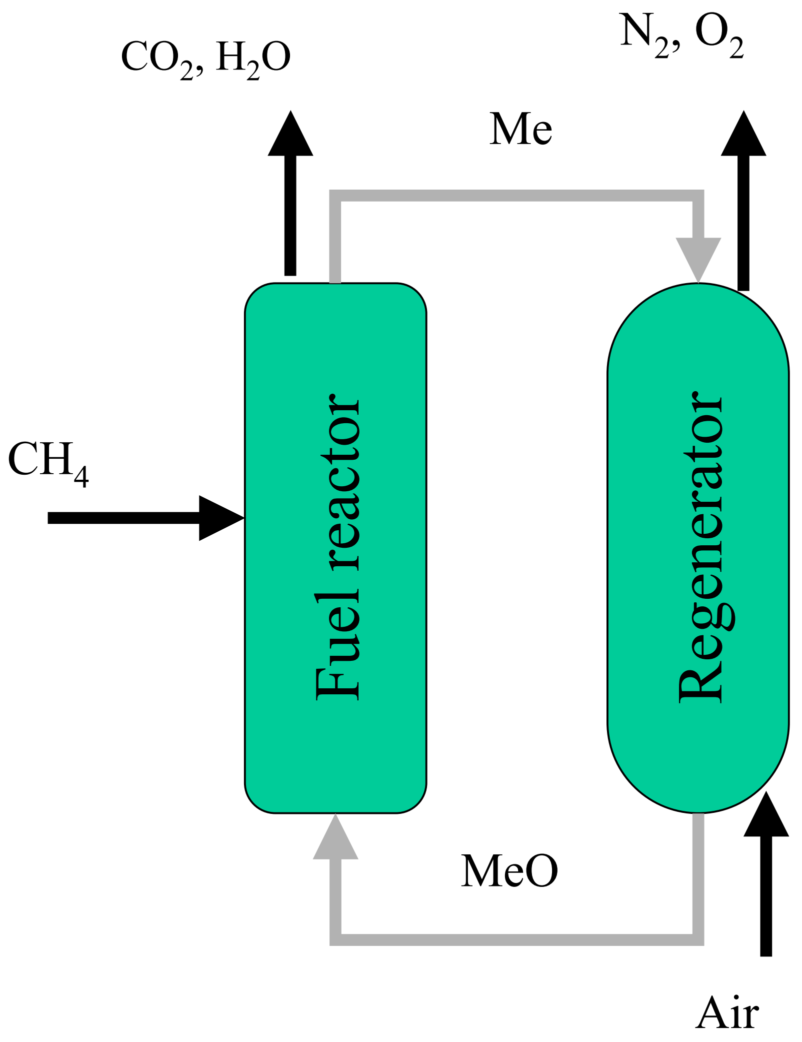
A grain from our synthetic sorbent showing pores in 5 - 50 nm range

e.g. Midgley, P.A., *Science*, **309**, 2195 (2005)

Example 2

Chemical Looping Combustion (CLC)

CHEMICAL LOOPING COMBUSTION - CH_4



Fuel Reactor:

$CH_4 + 4/y\ Me_xO_y \rightarrow 4x/y\ Me + CO_2 + 2H_2O$

Regenerator:

$4x/y\ Me + 2\ O_2 \rightarrow 4/y\ Me_xO_y$

Overall:

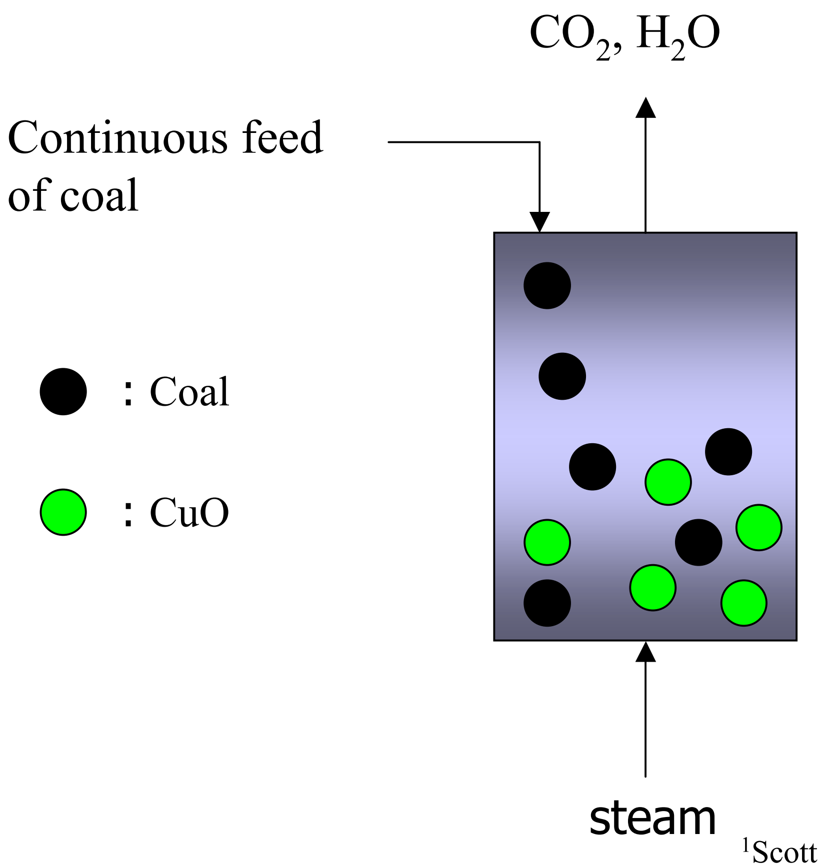
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

The exergetic efficiency of a plant using chemical looping combustion would be comparable with a conventional IGCC plant [1]

[1] Anhedens M., Svedberg G. (1998). Energy Convers. Mgmt, 39, 1967-1980.

CLC REACTION CYCLE (SOLID FUEL[1,2])

Step 1 : Continuous feeding



- Coal fed continuously & gasified by steam (or steam/CO_2) to form Syngas ($CO + H_2$)
- Syngas is oxidized by CuO in the bed.

$$\text{Coal} \xrightarrow{\textit{Steam gasification}} CO + H_2$$

$$H_2 + CO + 2CuO \rightarrow 2Cu + CO_2 + H_2O$$

- Balanced heat load

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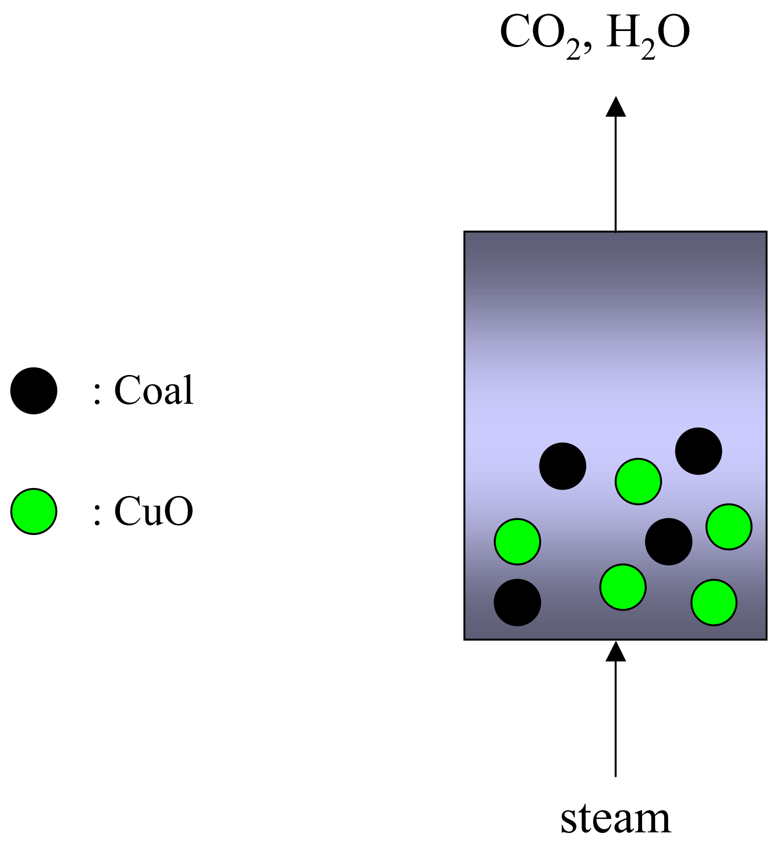
[1] Scott, S.A., Dennis, J.S., Hayhurst, A.N., & Brown, T. (2006). *A.I.Ch.E.J.*, **52**, 3325-3328.

[2] Dennis, J.S., Scott, S.A. & Hayhurst, A.N. (2006). *J. Inst. Energy*, **79**, 187-190. **79**, 187-190.

CLC REACTION CYCLE (SOLID FUEL)

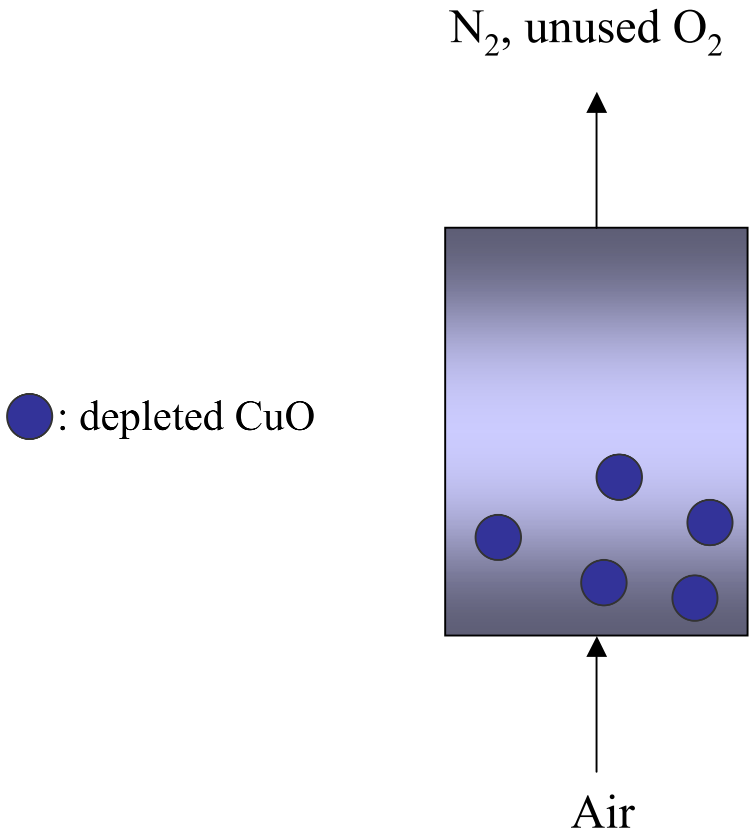
Step 2: Depletion of Inventory



- As CuO becomes exhausted the coal feeding is stopped
- The accumulated carbon inventory is allowed to gasify

CLC REACTION CYCLE (SOLID FUEL)

Step 3: Regeneration



- Fluidising gas is switched to air for regeneration of the oxygen carrier

$$Cu + 0.5O_2 \rightarrow CuO$$

- Exothermic

MATERIALS – COPPER OXIDE

Reduction

$2CuO_{(s)} + CO \rightarrow Cu_2O_{(s)} + CO_2$ $\Delta H = -142\ kJ\ mol^{-1}$

$2CuO_{(s)} + H_2 \rightarrow Cu_2O_{(s)} + H_2O$ $\Delta H = -120\ kJ\ mol^{-1}$

$Cu_2O_{(s)} + CO \rightarrow 2\ Cu_{(s)} + CO_2$ $\Delta H = -101\ kJ\ mol^{-1}$

$Cu_2O_{(s)} + H_2 \rightarrow 2\ Cu_{(s)} + H_2O$ $\Delta H = -71\ kJ\ mol^{-1}$

Re-oxidation

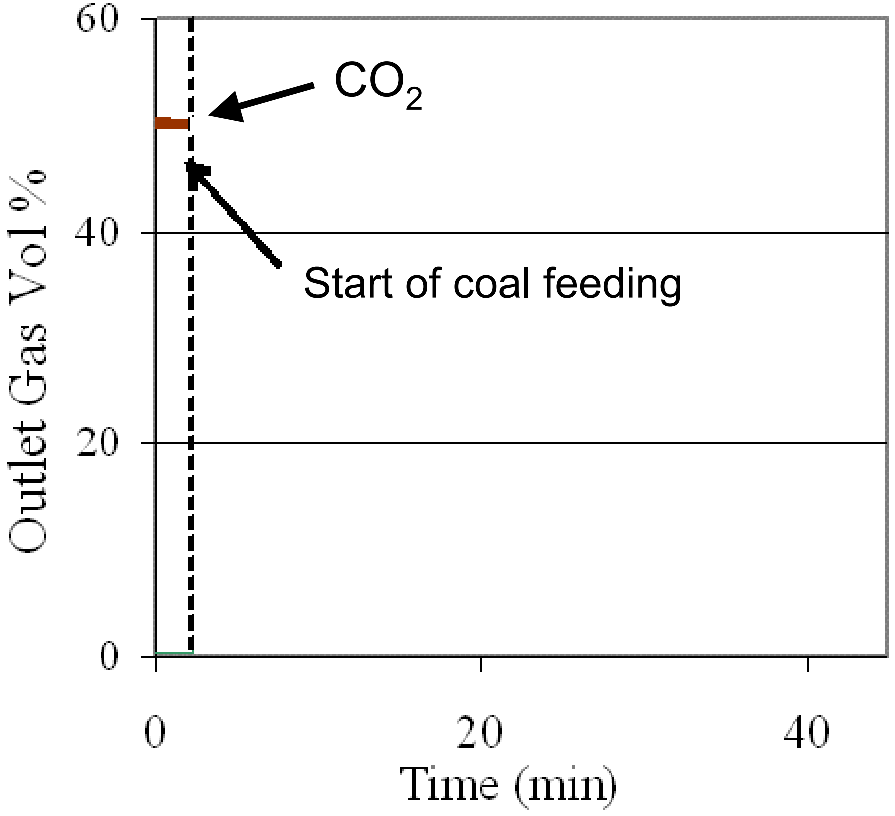
$2\ Cu_{(s)} + \frac{1}{2}O_2 \rightarrow 2\ Cu_2O_{(s)}$ $\Delta H = -171\ kJ\ mol^{-1}$

$Cu_2O_{(s)} + \frac{1}{2}O_2 \rightarrow 2CuO_{(s)}$ $\Delta H = -141\ kJ\ mol^{-1}$

- Large amount of heat released in both oxidation *and* reduction
- The form of the oxide is key to longevity – we have found that co-precipitated CuO on Al_2O_3 gives porous, highly-reactive particles with long lifetime

ILLUSTRATION: CLC WITH CONTINUOUS FEEDING OF LIGNITE IN A LABORATORY FLUIDISED BED

- Inert Bed of Silica Sand



- Bed fluidised by 50% CO$_2$ in N$_2$
- Temperature 820°C

CLC WITH CONTINUOUS FEEDING OF LIGNITE

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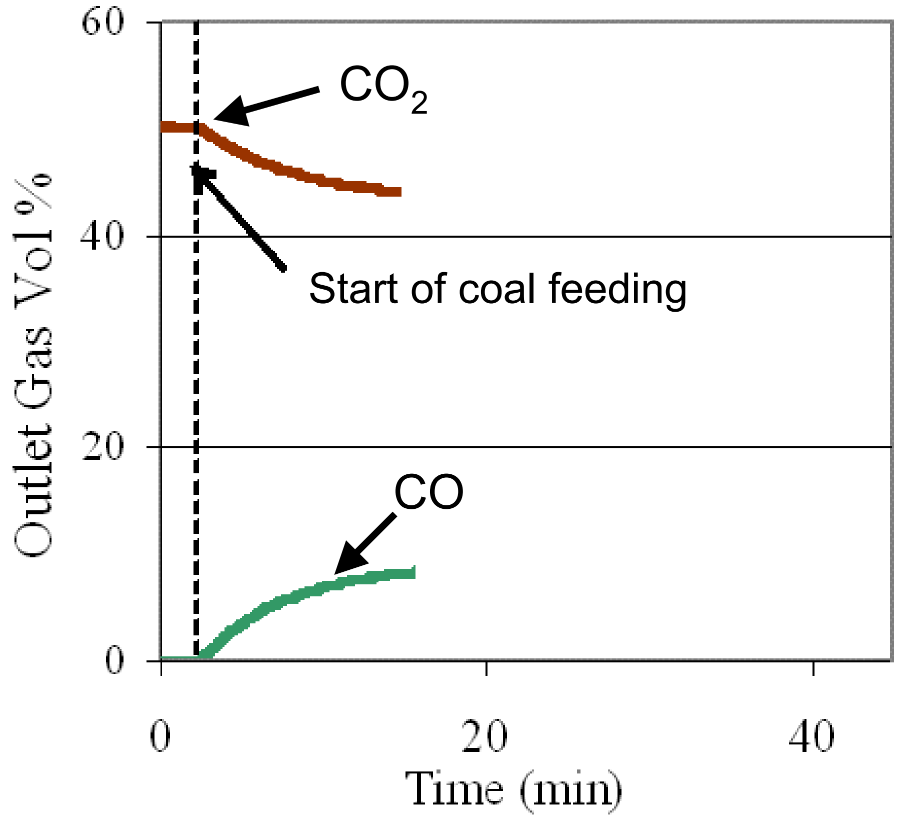

- Gasification: $C + CO_2 \rightarrow 2CO$

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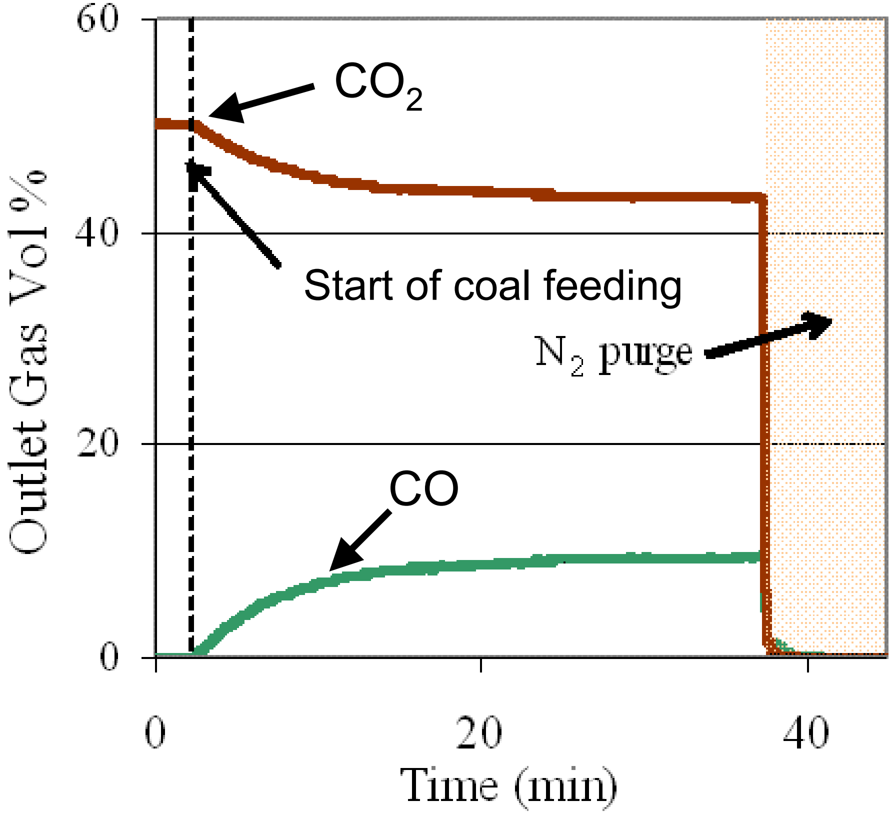

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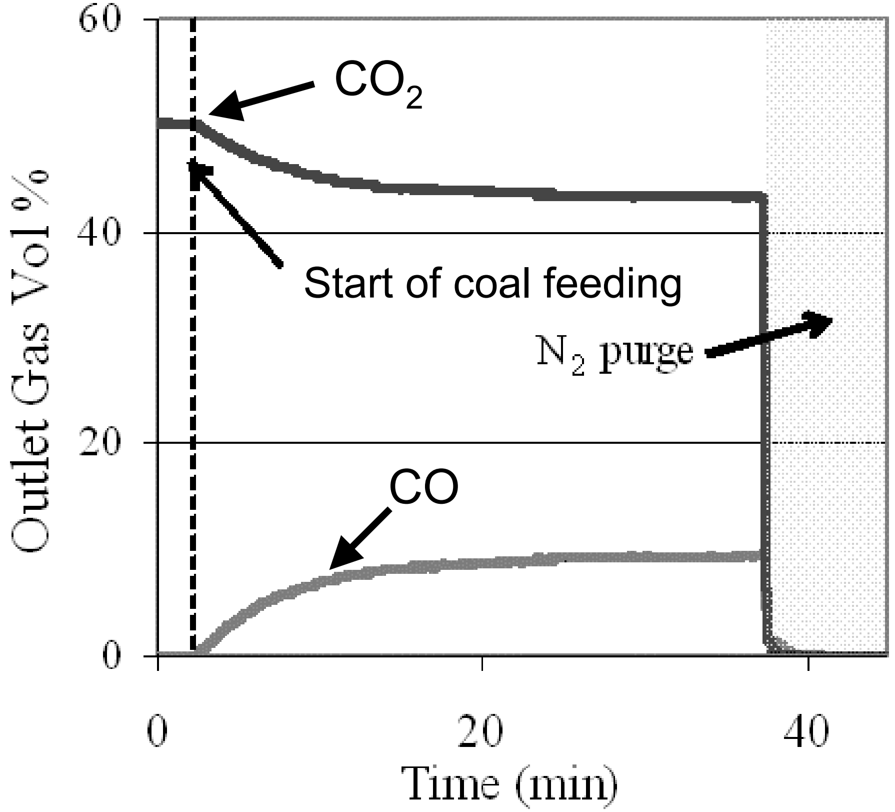
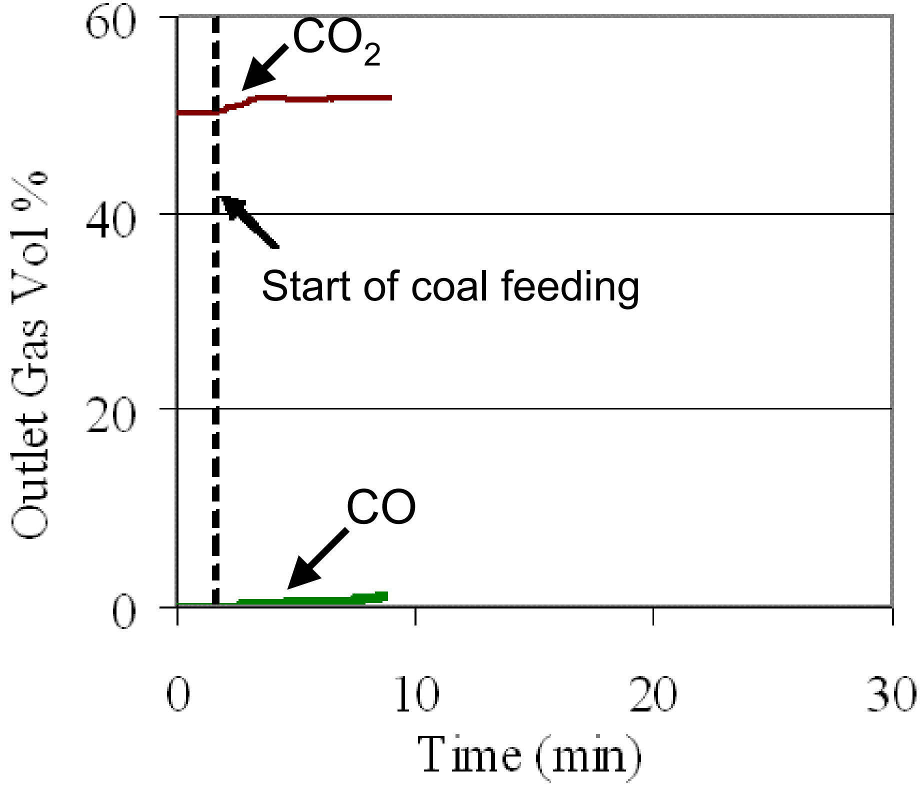


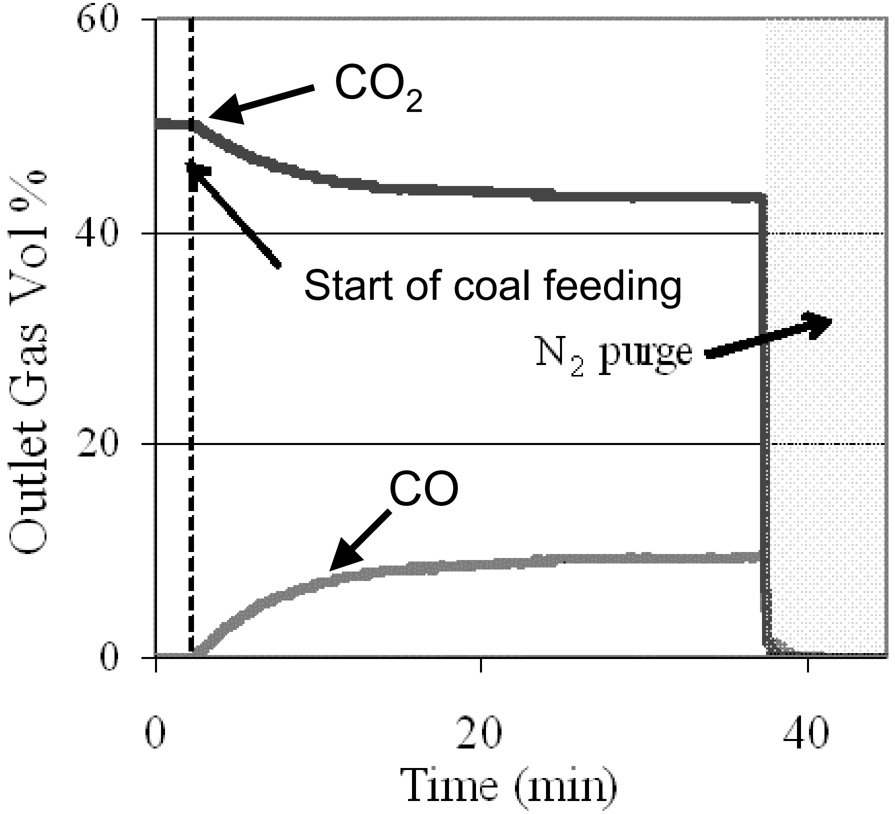
- Active Bed of CuO



- $C + CO_2 \rightarrow 2CO$
- $CO + CuO \rightarrow CO_2 + Cu$

CLC WITH CONTINUOUS FEEDING OF LIGNITE

- Inert Bed of Silica Sand



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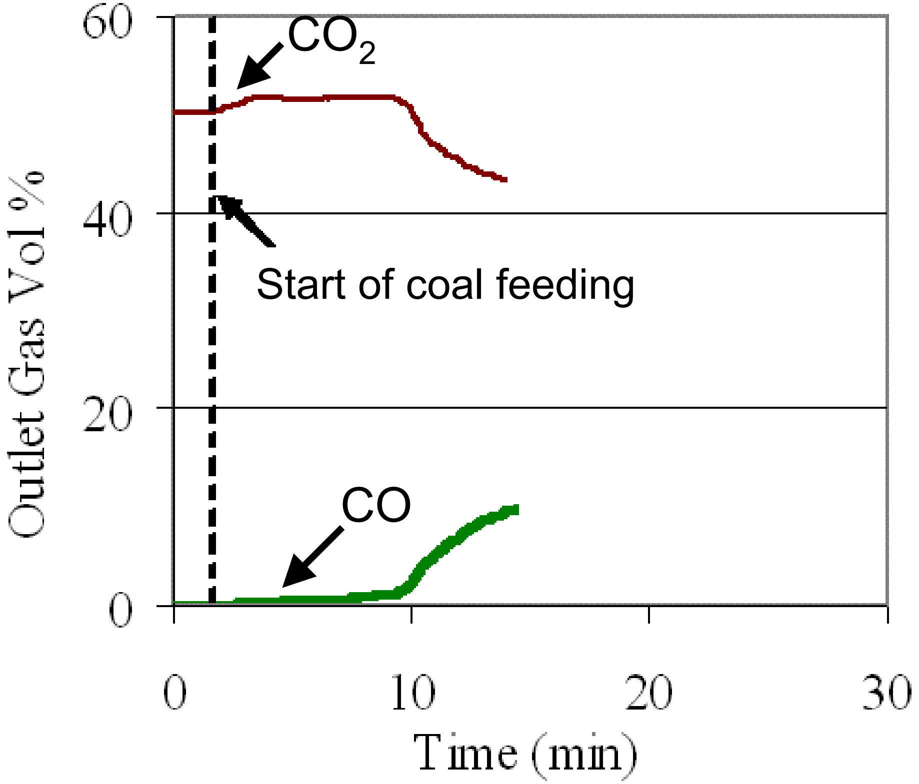

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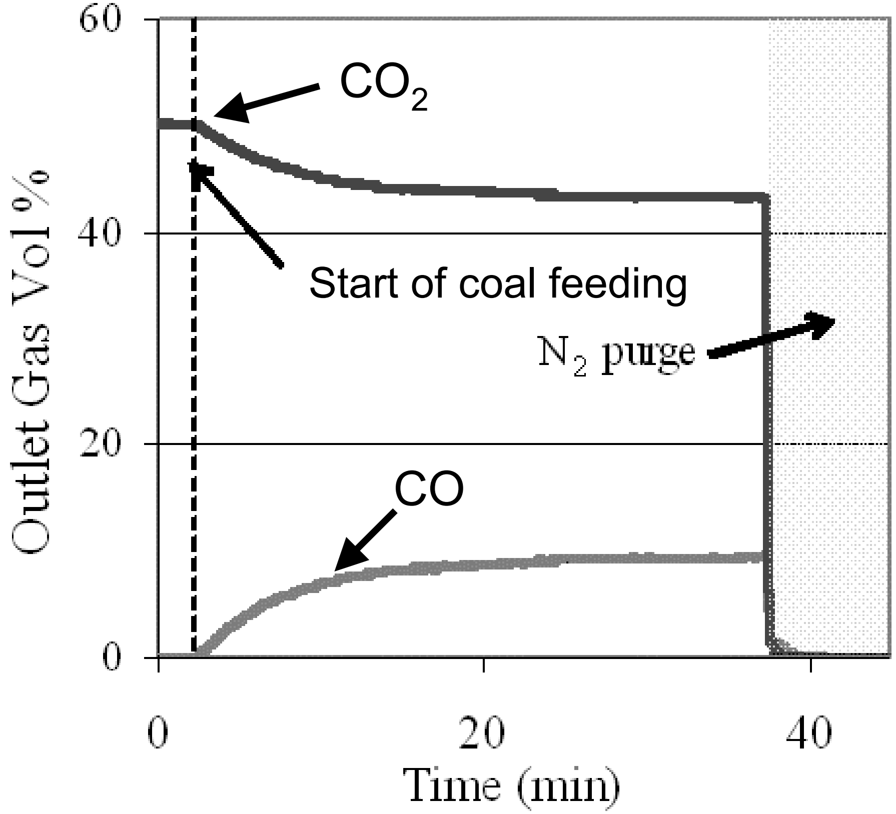

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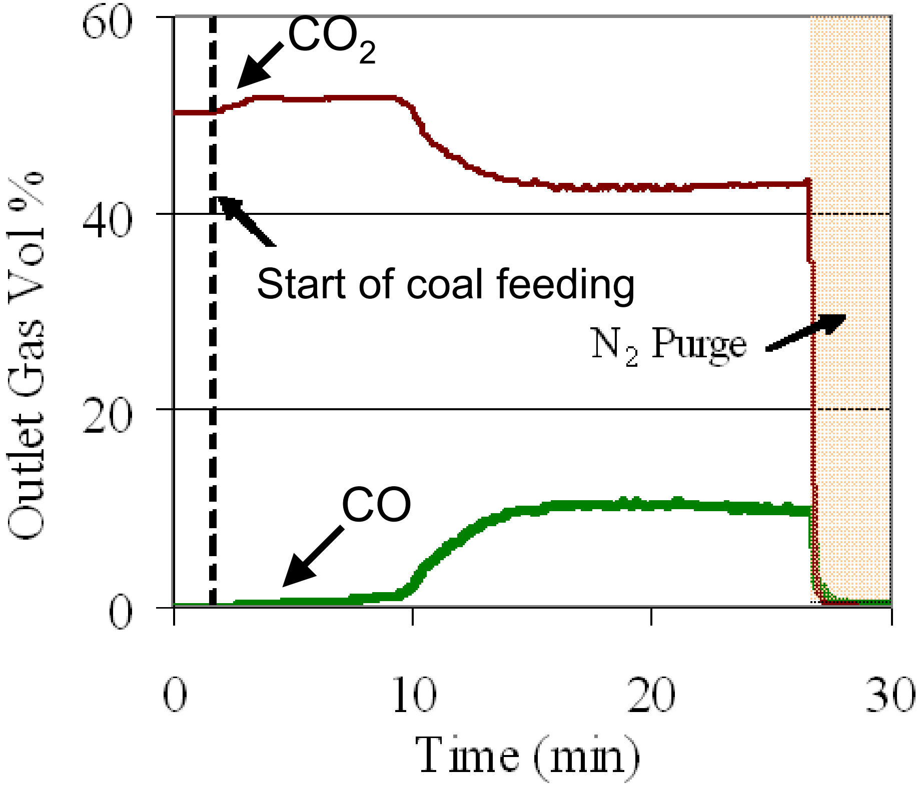

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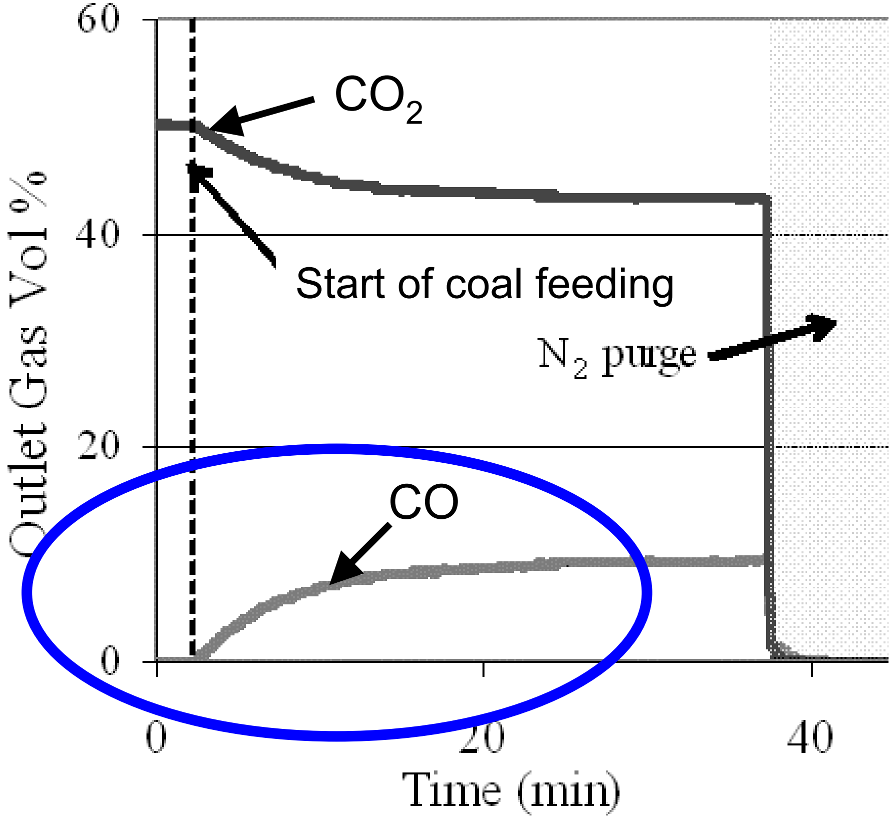

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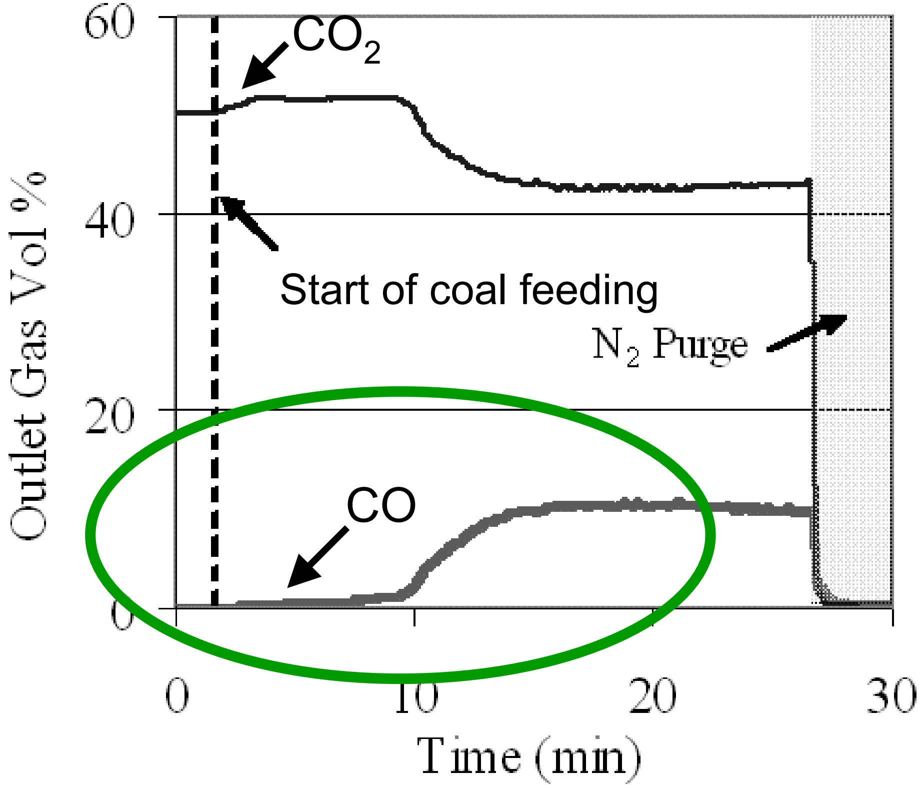
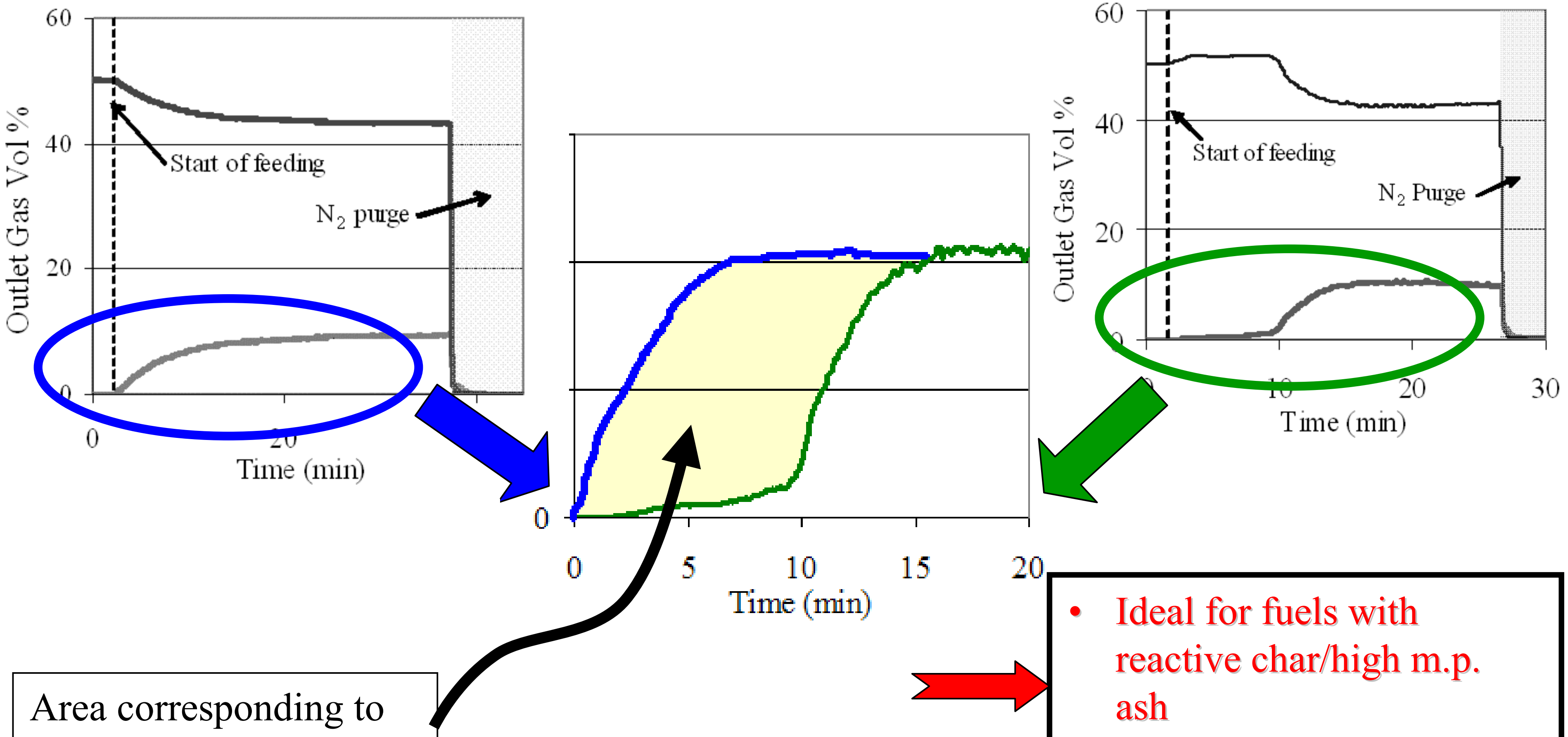


- Comparing CO curves…

CLC WITH CONTINUOUS FEEDING OF LIGNITE

- Inert Bed of Silica Sand
- Active Bed of CuO



Area corresponding to CO reacted with CuO

- Ideal for fuels with reactive char/high m.p. ash
- Effect of S in coal unclear

Example 3:

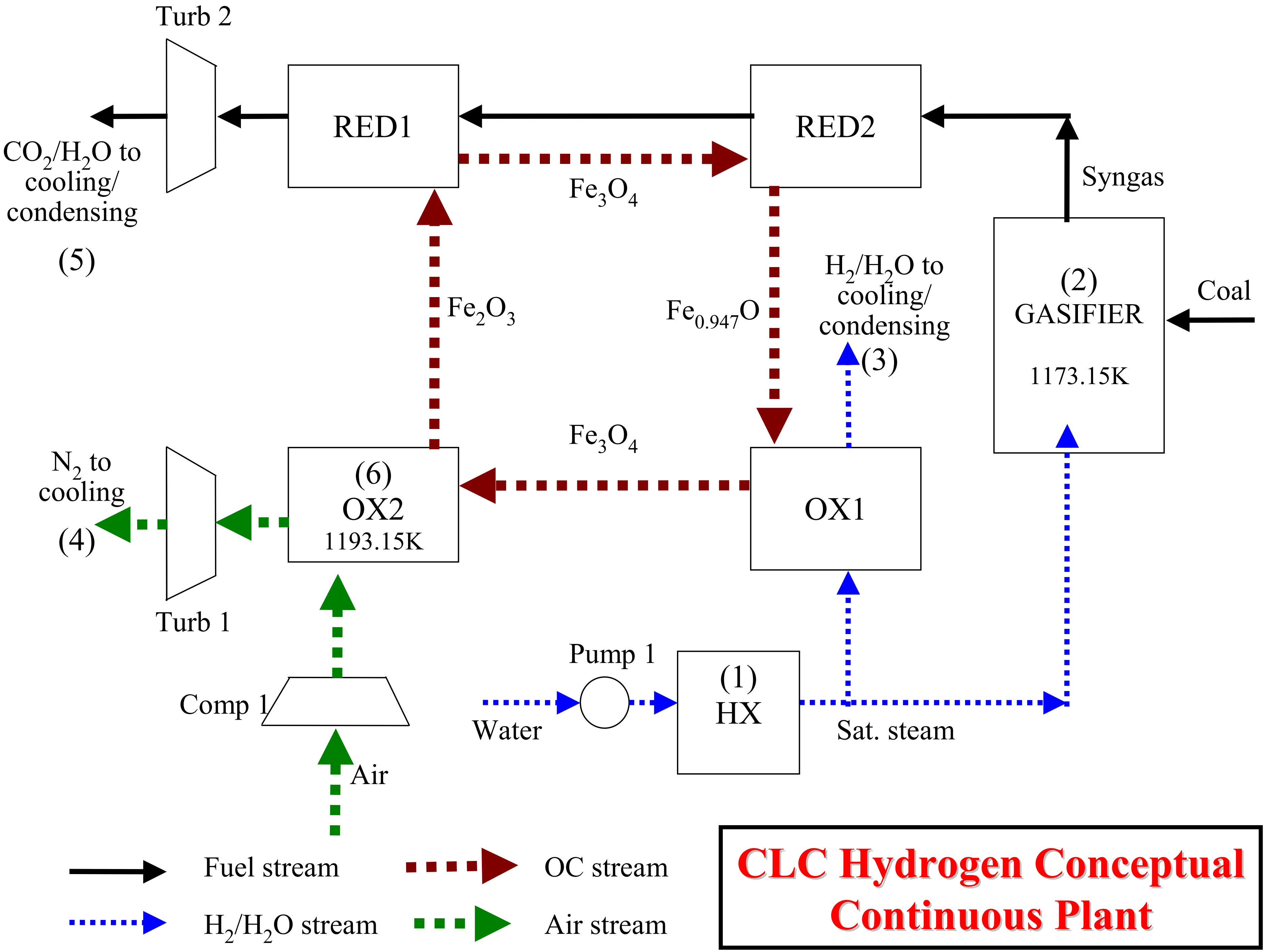
CLC Hydrogen Production and CO_2 Separation

CLC - The Iron Cycle and H_2 Generation

Reducing Reactions with Crude Syngas (CO + H_2 + tars)	ΔH^0_{1173K} kJ/mol	ΔG^0_{1173K} kJ/mol
$3Fe_2O_3(s) + CO(g) \rightarrow 2Fe_3O_4(s) + CO_2(g)$ (1)	-38.6	-108.2
$0.947Fe_3O_4(s) + 0.788CO(g) \rightarrow 3Fe_{0.947}O(s) + 0.788CO_2(g)$ (2)	+16.7	-5.5
$3Fe_2O_3(s) + H_2(g) \rightarrow 2Fe_3O_4(s) + H_2O(g)$ (3)	-5.5	-110.6
$0.947Fe_3O_4(s) + 0.788H_2(g) \rightarrow 3Fe_{0.947}O_4(s) + 0.788H_2O(g)$ (4)	+42.8	-7.3

Oxidising Reactions with Steam (5) and Air (6)	ΔH^0_{1173K} kJ/mol	ΔG^0_{1173K} kJ/mol
$3Fe_{0.947}O_4(s) + 0.788H_2O(g) \rightarrow 0.947Fe_3O_4(s) + 0.788H_2(g)$ (5)	-42.8	+7.3
$2Fe_3O_4(s) + 0.5O_2(g) \rightarrow 3Fe_2O_3(s)$ (6)	-243.3	-72.4

Complicated thermodynamics!



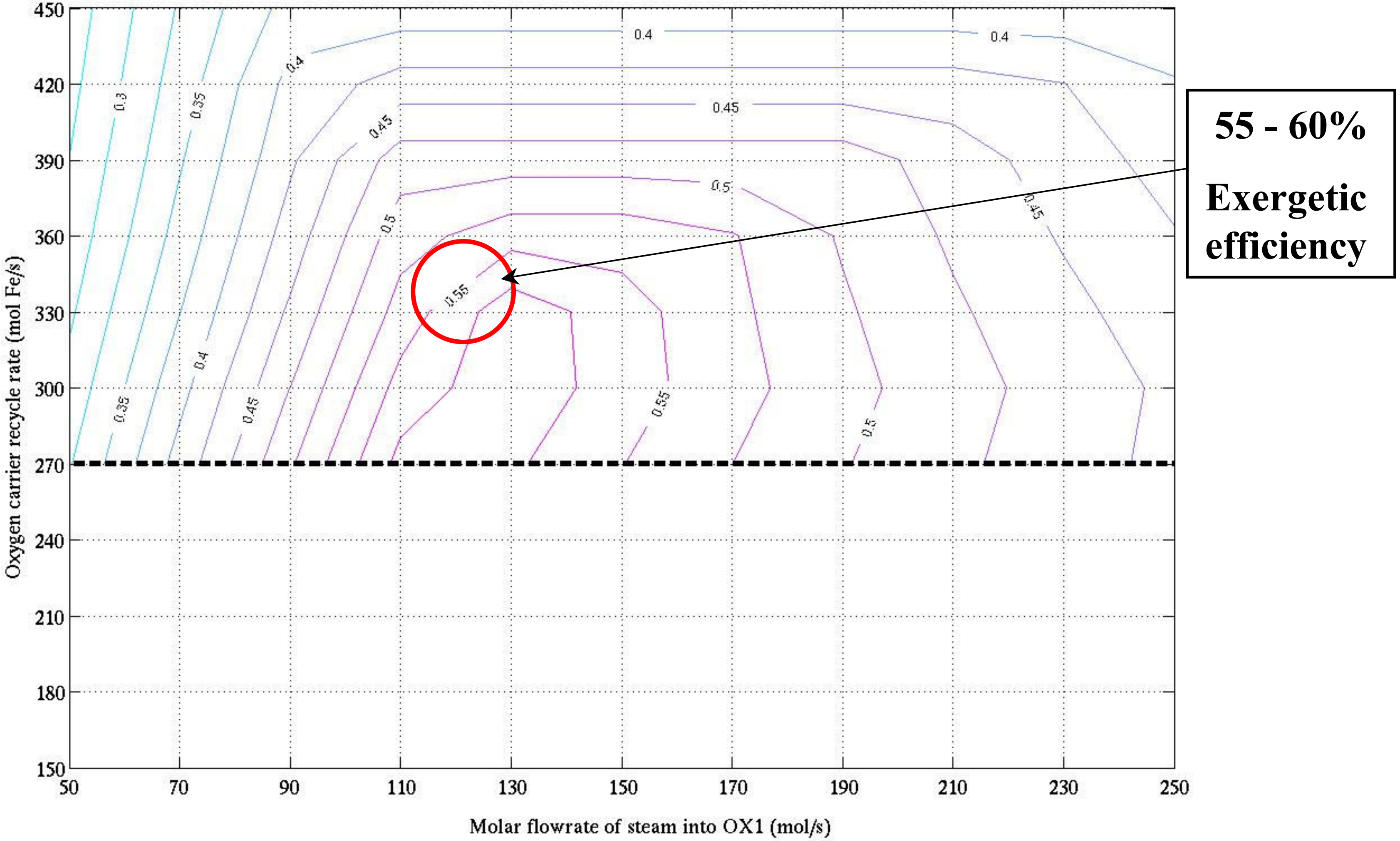
CLC Hydrogen Conceptual Continuous Plant

CLC - The Iron Cycle and H_2 Generation

- Suitable for range of scales for H_2 production
- H_2 production uncoupled from syngas production
- Upgrades low grade syngas to high grade H_2, free of CO_x
- Suppose the coal is gasified with pure CO_2.
- $C_{(s)} + H_2O_{(g)} + 2.38\,(0.21O_{2(g)} + 0.79N_{2(g)}) \rightarrow$

  $CO_{2(g)} + H_{2(g)} + 1.88N_{2(g)}$; $\Delta H = -151\ \text{kJ mol}^{-1}$
- So, by suitable heat integration one could produce separate streams of CO_2, H_2 and export some heat.
- Pressurised operation possible.

CLC - Hydrogen: Exergetic Efficiency of Continuous Plant (J. Cleeton/S. Scott) - 10 bar pressure



55 - 60%

Exergetic efficiency

Example 4:

MRI and Discrete Element Modelling to Investigate Scale-Up

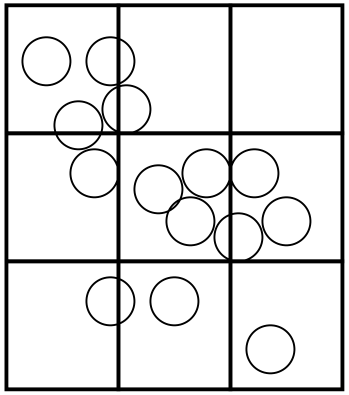
DISCRETE ELEMENT MODELLING (DEM)

- Started with wanting to understand devolatilising particles - biomass gasification/combustion (Birmingham/Cambridge)
- Trajectory of *each* particle is considered separately
- Motion of each particle:

$$m_i \frac{d\underline{v}_i}{dt} = \sum \underline{F}$$

$$I_i \frac{d\underline{\omega}_i}{dt} = \sum \underline{M}$$

Spatial decomposition
(neighbour particles)



after Thornton and Kafui

PARTICLE-FLUID COUPLING

Continuity (volume averaged):

$$\frac{\partial \varepsilon\rho}{\partial t} + \nabla \cdot (\varepsilon\rho\mathbf{u}) = 0$$

Momentum equation (volume averaged):

$$\frac{\partial(\varepsilon\rho\mathbf{u})}{\partial t} + \nabla \cdot (\varepsilon\rho\mathbf{u}\mathbf{u}) = -\nabla \cdot S - \mathbf{F}_{\mathrm{fp}} + \varepsilon\rho\mathbf{g}$$

$$\mathbf{F}_{\mathrm{fp}} = \overset{\text{Buoyancy}}{\boxed{-(1-\varepsilon)\nabla \cdot S}} + \overset{\text{drag}}{\boxed{n\mathbf{f}_{\mathrm{d}}}}$$

Anderson & Jackson (1967)

$$\nabla \cdot S = -\nabla p + \nabla \cdot \tau$$

(n - no. of particles in volume)

Particle:

$$m_i \frac{d\mathbf{v}_{\mathrm{i}}}{dt} = \mathbf{f}_{\mathrm{ci}} + \mathbf{f}_{\mathrm{fpi}} + m_i\mathbf{g}$$

$$\mathbf{f}_{\mathrm{fpi}} = \overset{\text{Buoyancy …}}{\boxed{-V_{pi}\nabla p + V_{pi}\nabla \cdot \tau}} + \overset{\text{drag}}{\boxed{\mathbf{f}_{\mathrm{di}}}}$$

THEORY AND EXPERIMENT in CFBC SCALE-UP

- Circulating Fluid. Beds (CUED/Chem Eng/TU Hamburg)
  - oxyfuel firing: modelling of particle motion/reaction

Müller, Dennis, Gladden *et al.* (2007). *ICMF 2007*, Leipzig

Müller, Dennis, *et al.* (2006). *Phys. Rev. Letters*, 96, 15404-1 to 15404-4.

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