The oxygen carrier
–
the key to unlock CO_2 capture at low cost and low energy penalty

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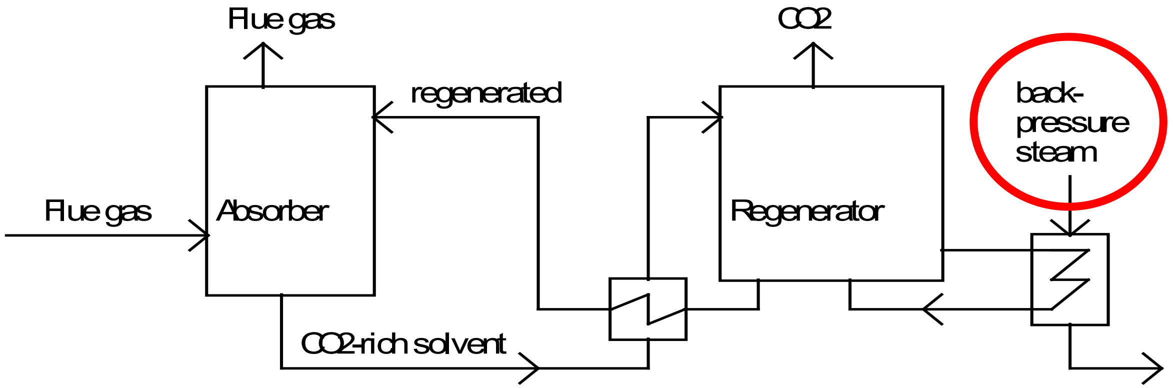
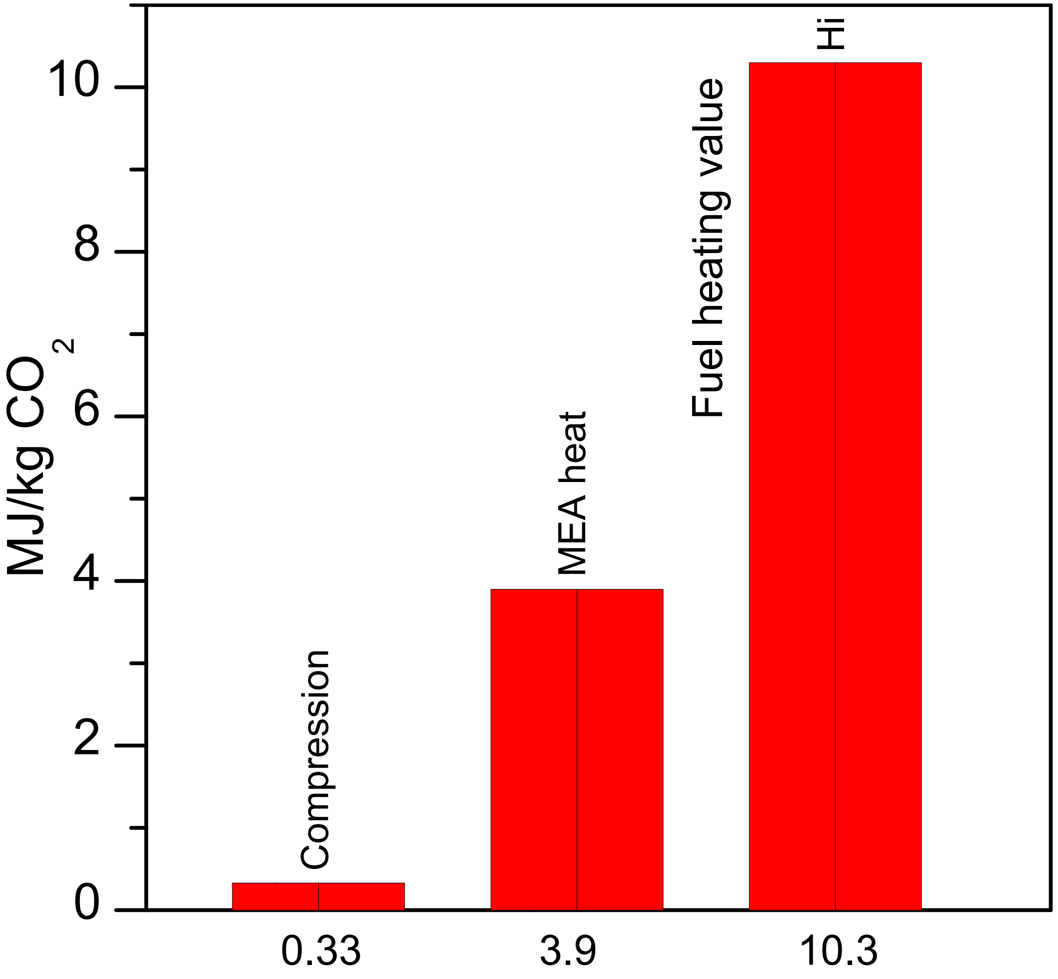
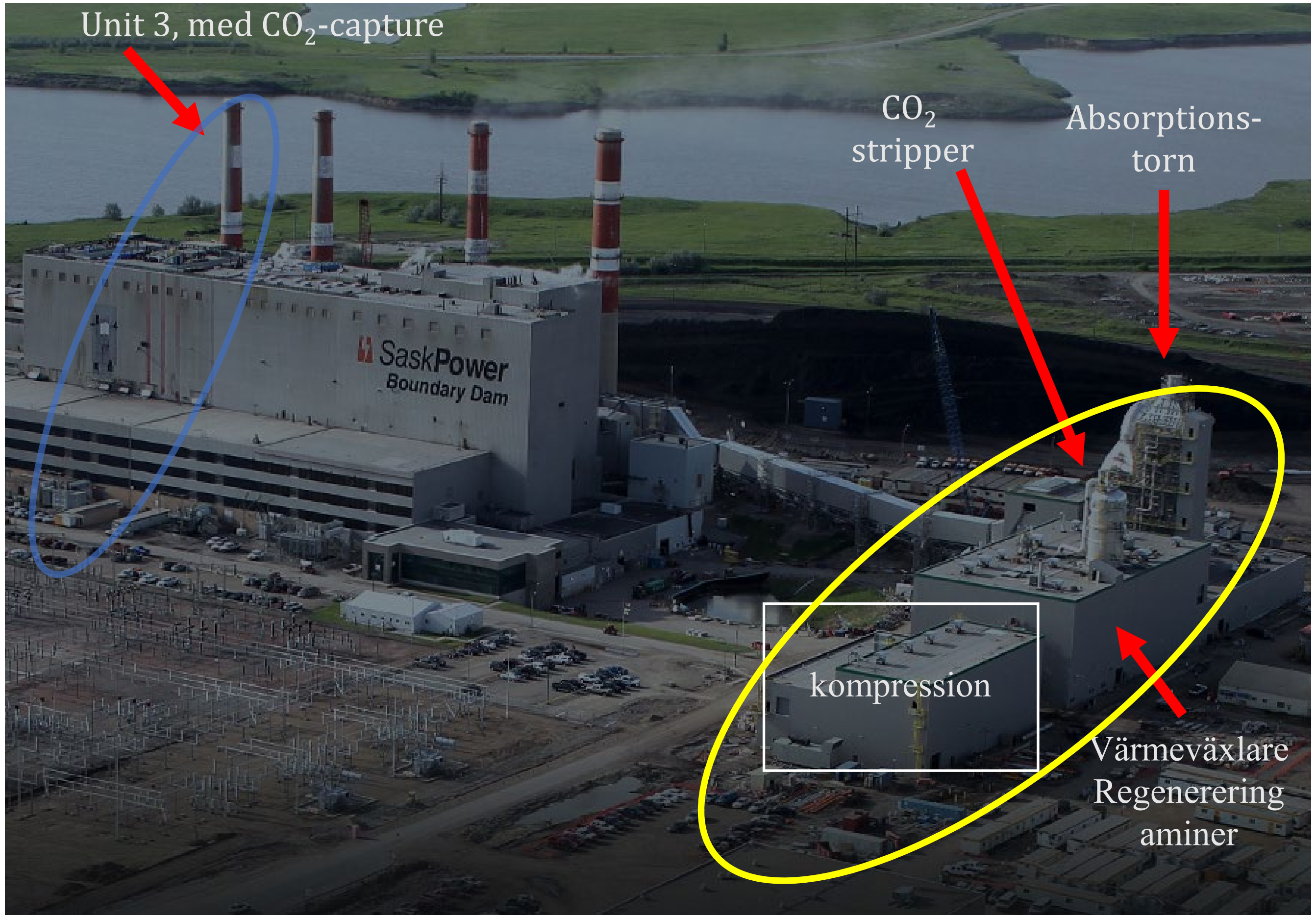
Absorption of CO_2 med monoethanolamine (MEA)





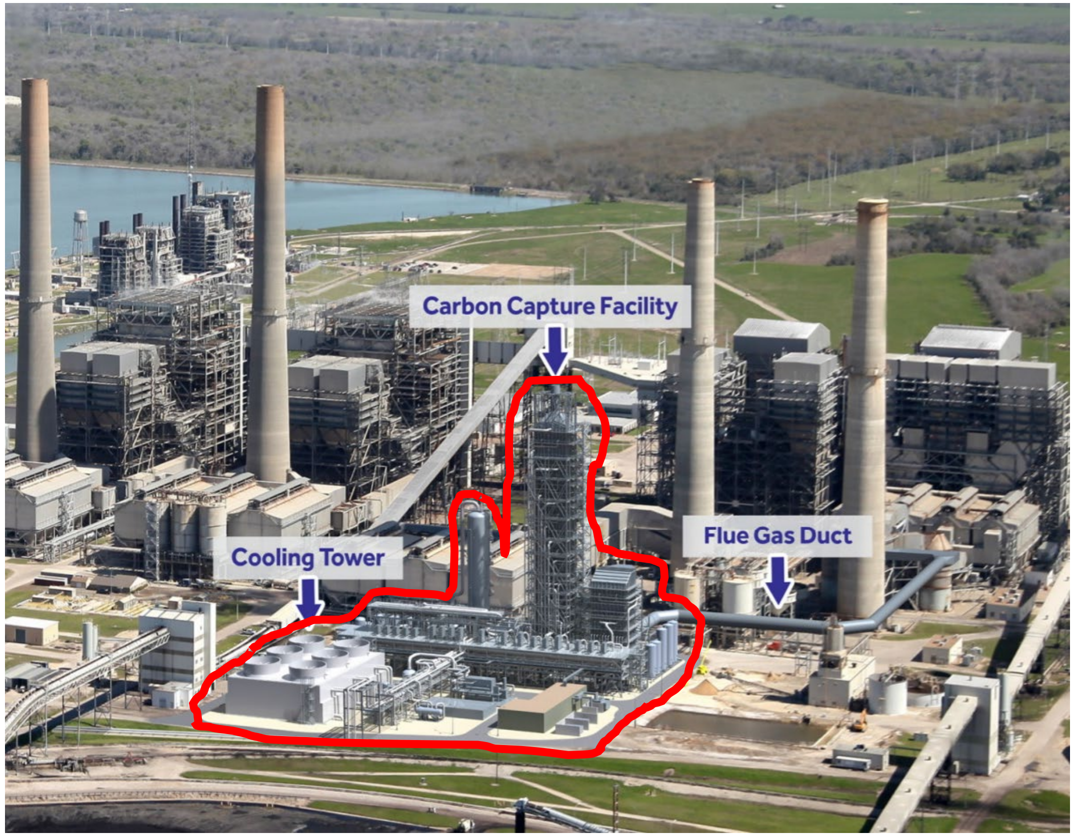
Status CCS

Boundary Dam, Unit 3, 110 MW, 1 MtCO_2/year, start 2014



Capture: 0.62 Mt/year first 6.5 years

Petra Nova, 1.4 Mt/year, start 2017



Shut down 2020

Large cost for equipment, operation and energy.

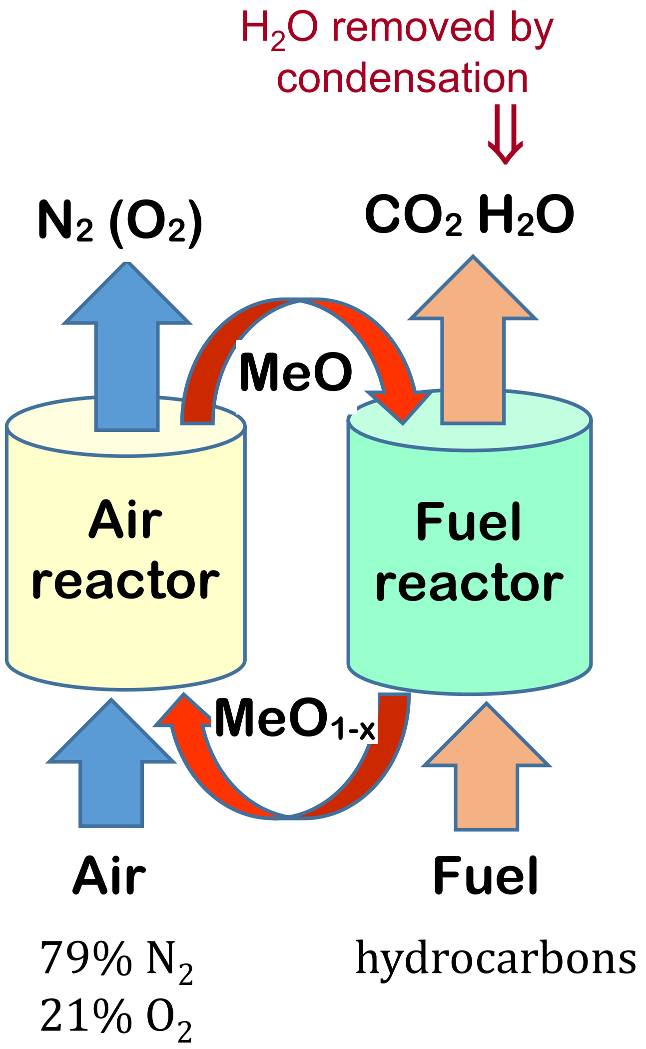
Chemical-Looping Combustion (CLC)

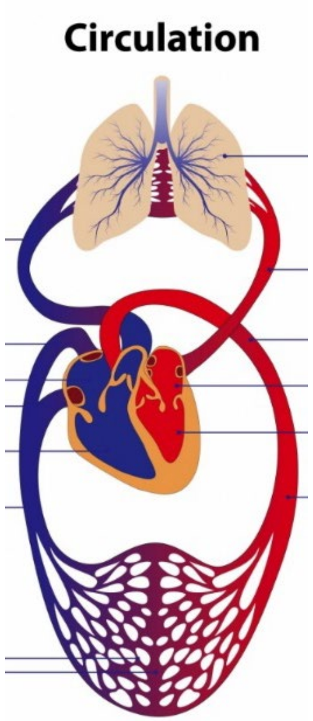
Oxygen is transferred from air to fuel by *metal oxide particles:* **the oxygen carrier**

Inherent CO_2 capture:

- fuel and combustion air *never mixed*
- ***no active gas separation needed***

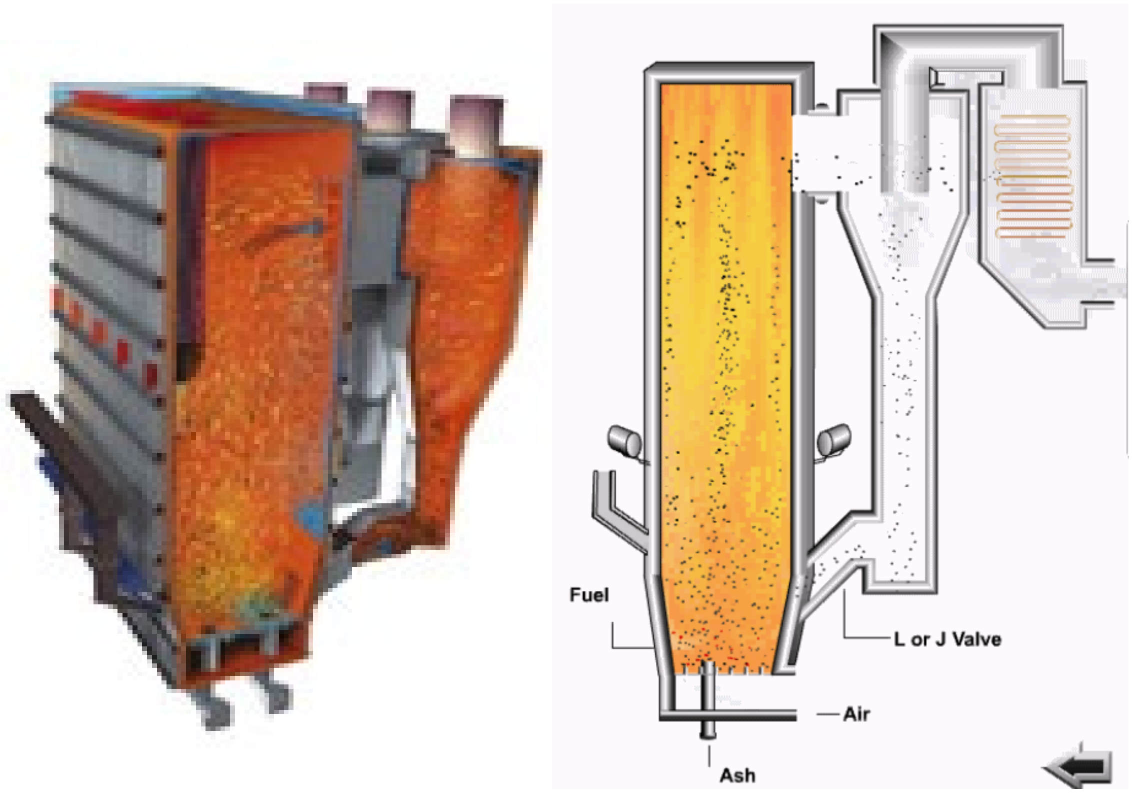
<u>Unique</u> potential for reducing costs of CO_2 capture!



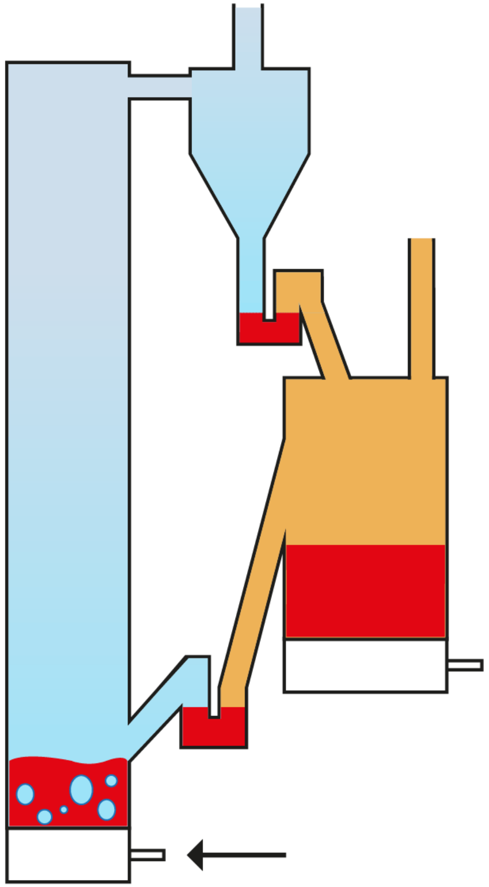


High similarity between Chemical Looping Combustion and Circulating Fluidized-Bed (CFB) boilers

Circulating fluidized-bed boiler
(commonly used for solid fuels)



Chemical Looping Combustion



But, does it work in practice ?

Yes, it works!!

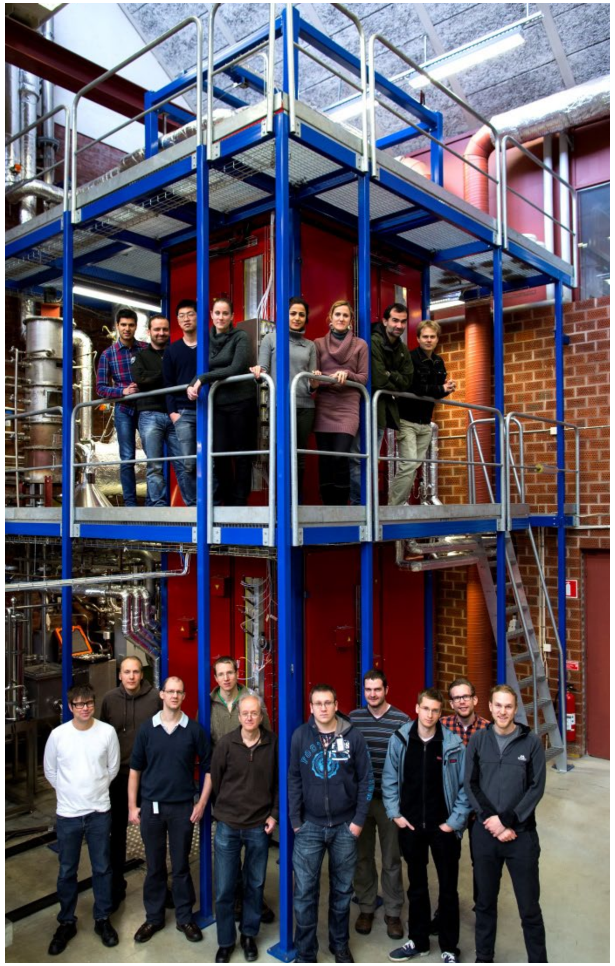
Total chemical-looping operation at Chalmers: 4 200 h in four pilots

Worldwide: >12 000 h in >50 pilots

10 kW gas, 2003

300 W gas, 2004

10 kW solid fuel, 2006



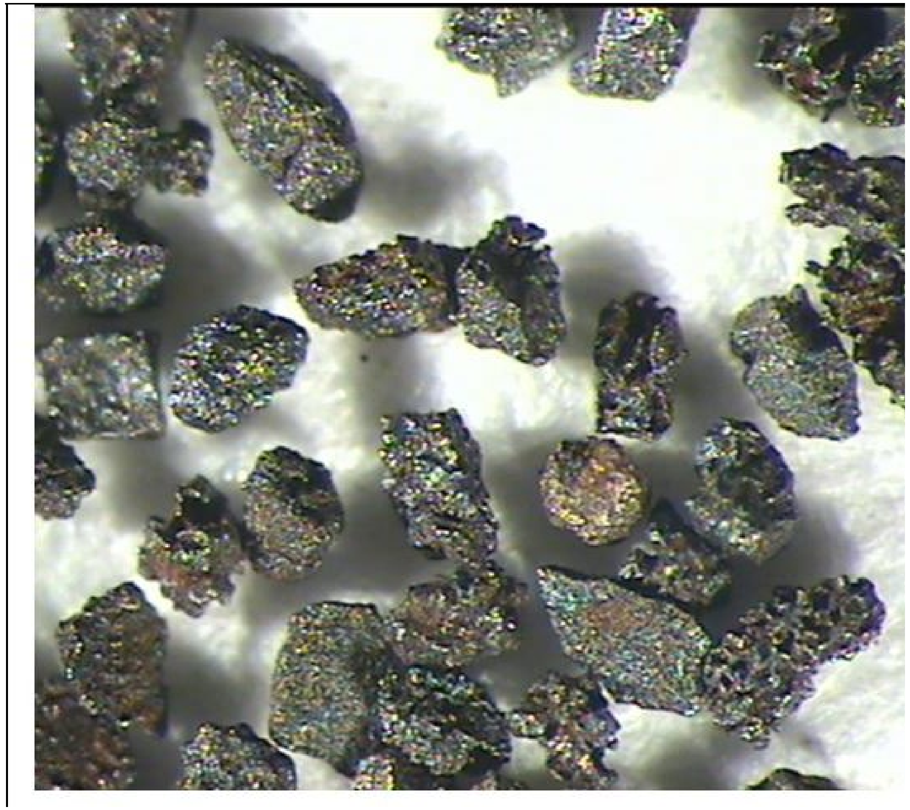
100 kW solid fuel, 2011

The <u>oxygen carrier</u> is the blood of CLC

Metal oxide particles of size 0.1-0.3 mm.

Operational temperature in CLC is typically 850 – 1100°C

Needed properties:
- Adequate reactivity
- Adequate thermodynamic properties
  - Reduced form must be able to oxidize in ≈4% O2
  - Oxidized form must be able to oxidize fuel (≈100%)
- Particle integrity
  - Resistant to formation of fines
  - Low risk of agglomeration
  - Maintain reactivity
  - Low risk w.r.t. HSE (Health & Safety & Environment)
  - Interaction (negative/positive) with ash and other contaminants (fuel-N, fuel-S) in case of solid fuels
- Reasonable cost



Manganese ore particles used in CLC.
Size fraction 0.18-0.21 mm

Examples of systems (oxidized↔reduced):
- Fe_2O_3↔Fe_3O_4; Mn_3O_4↔MnO; CuO↔Cu_2O/Cu; NiO↔Ni
- $Fe_2TiO_5+TiO_2$↔$FeTiO_3$; $(Mn,Fe)_2O_3$↔$(Mn,Fe)_3O_4$; $Mn_7SiO_{12}+SiO_2$↔$MnSiO_3$; Mg_2MnO_4↔$MgMn_2O_4+MgO$

Classes of oxygen carriers

Manufactured monometallic oxygen carriers

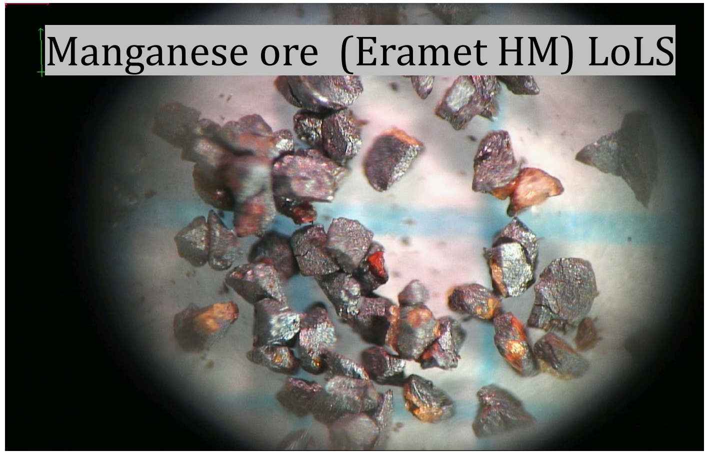
Iron oxide

Manganese oxide

*Copper oxide**

~~Nickel~~ oxide

(~~Cobalt~~ oxide)



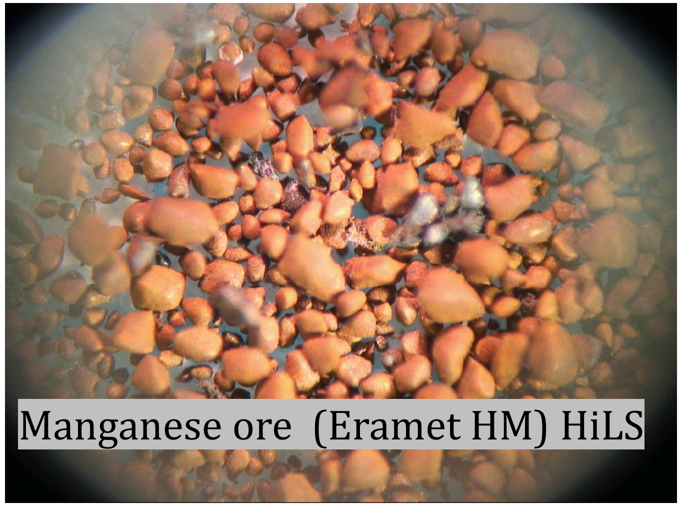
Natural ores and waste materials

Ilmenite ($FeTiO_3$)

Manganese ore

Iron ore

Fe-containing waste mtrls: Red mud, LD-slag, scales



Manufactured combined oxides

*Bimetallic combined Mn-materials**

$CaMn_{1-x}Mx_xO_{3-\delta}$ (Mx=Ti,Fe,Mg...)

Mn-Fe

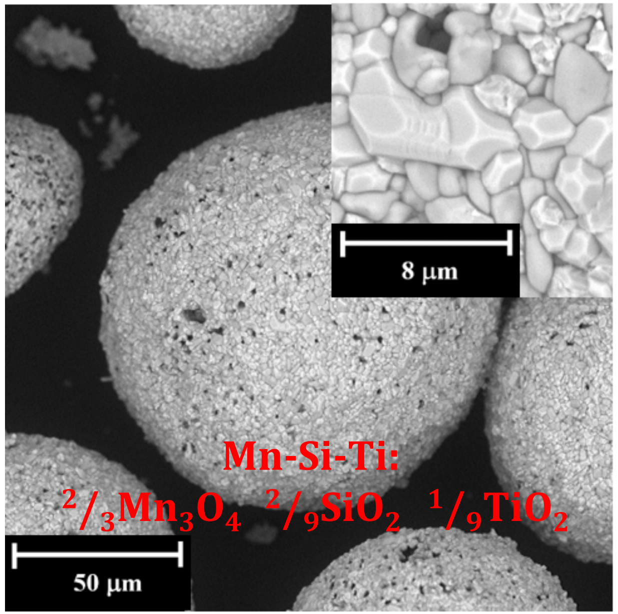
Mn-Mg

Mn-Si

. . .

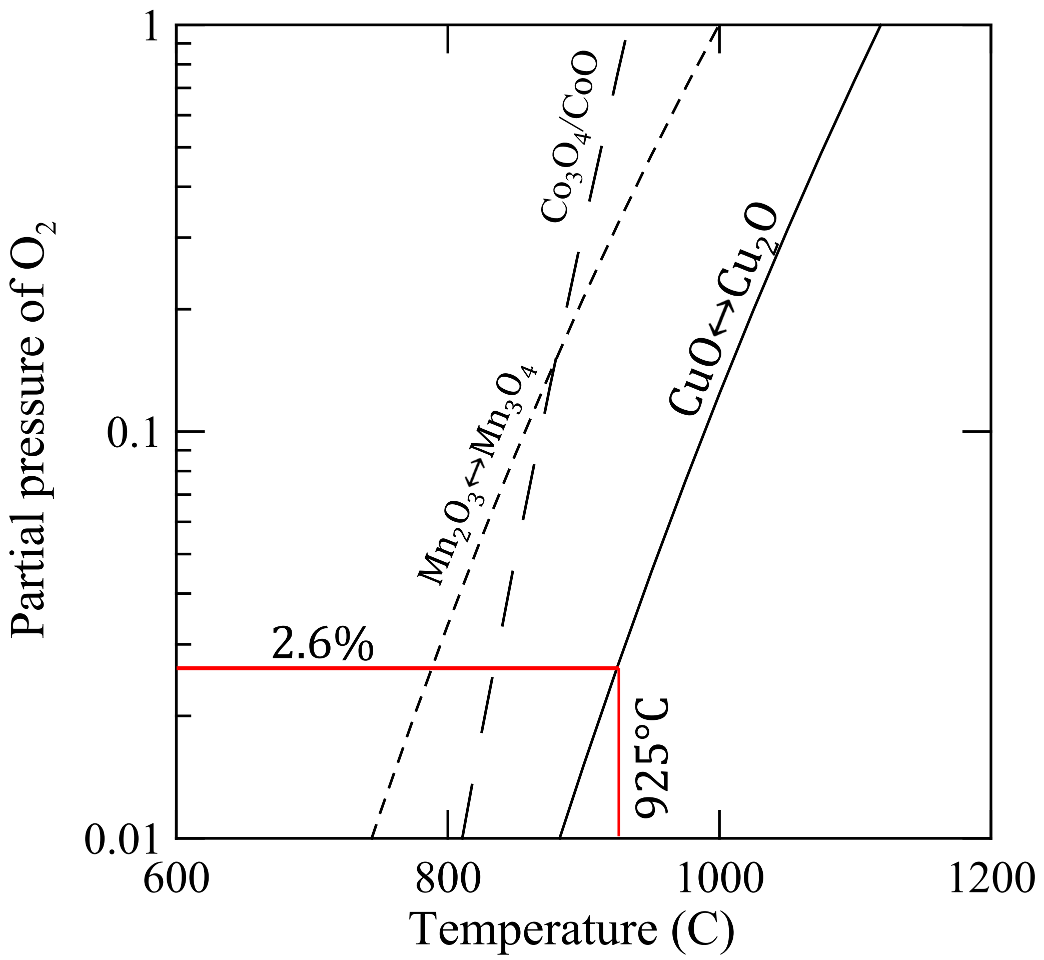
*Ternary Mn-materials**

Mn-Si-Ti, Mn-Ca-Mg, Mn-Ca-Si, Mn-Ca-Fe, Mn-Fe-Mg, Mn-Fe-Si, Mn-Si-Mg

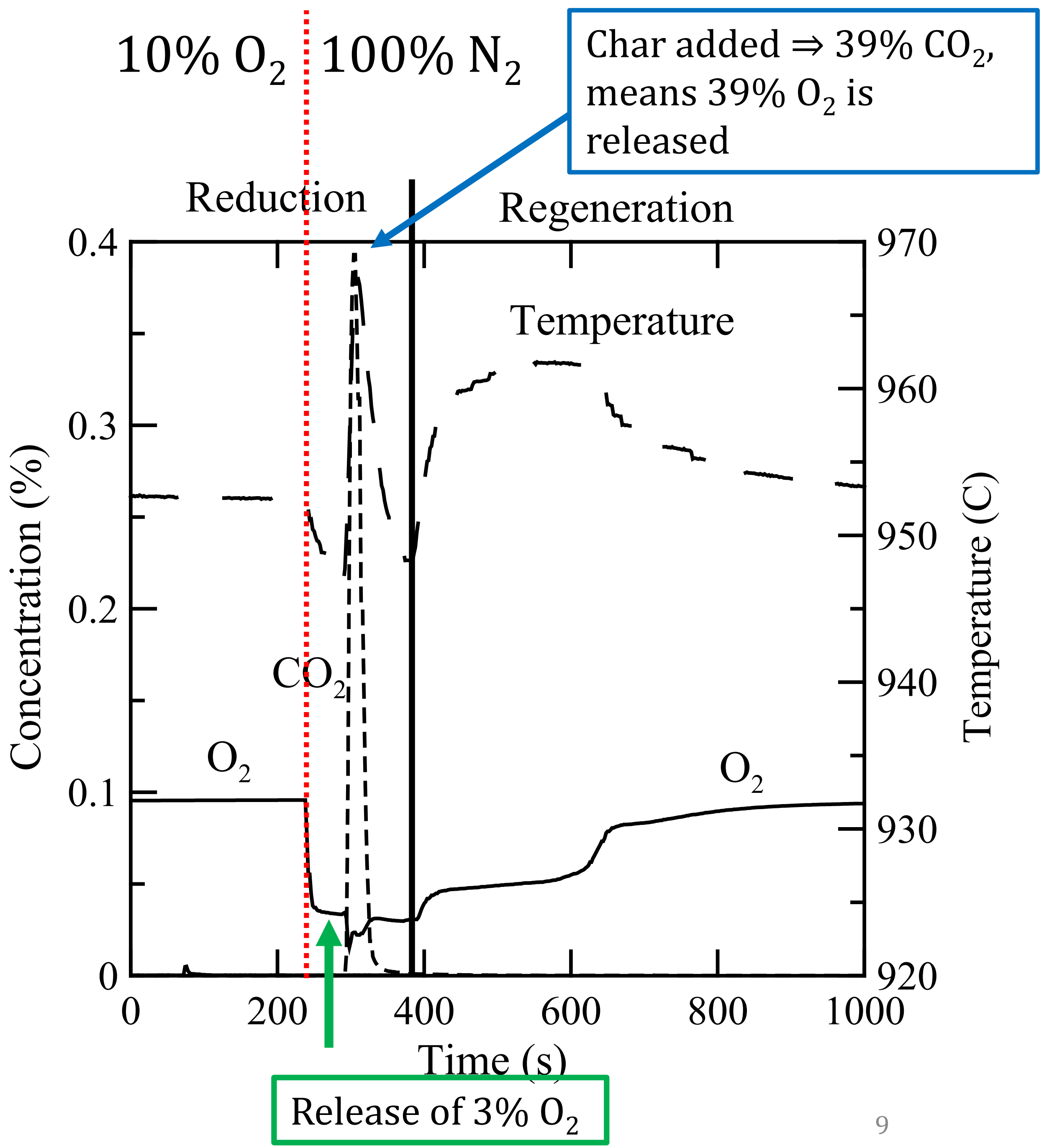


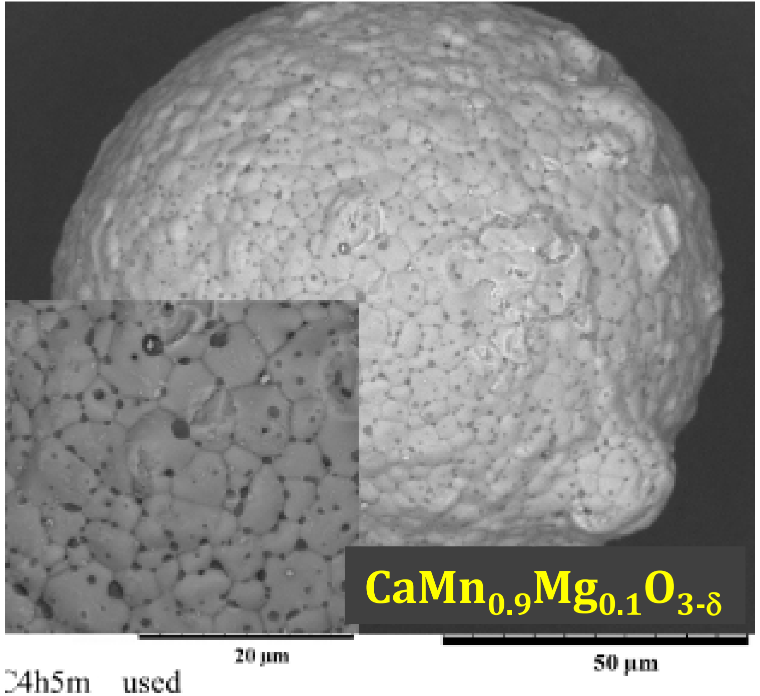
*CLOU materials (releases gas-phase oxygen)

CLOU (Chemical-Looping with Oxygen Uncoupling)

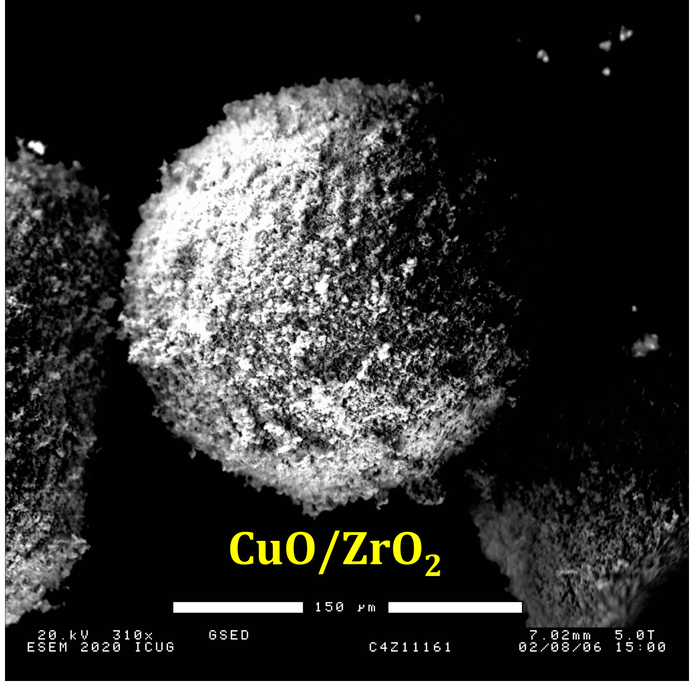


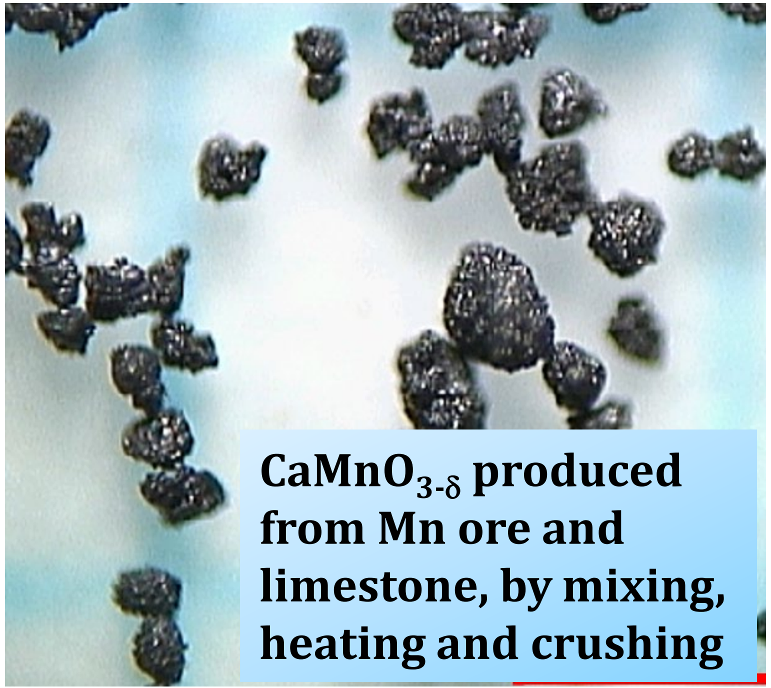
CuO↔Cu_2O equilibrium O_2 at 925°C 2.6%



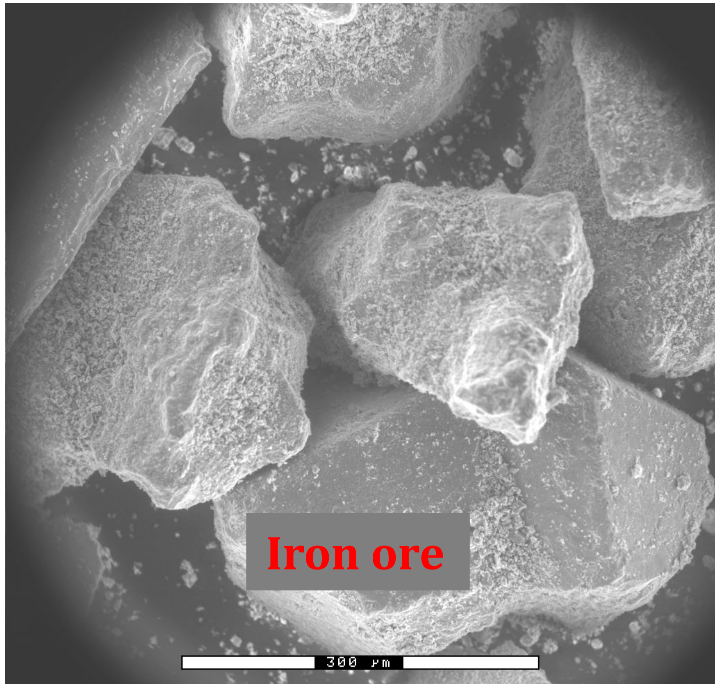

$CaMn_{0.9}Mg_{0.1}O_{3-\delta}$
20 µm
50 µm
used


Ilmenite ore (fresh)
150 µm


CuO/ZrO_2
150 µm


$CaMnO_{3-\delta}$ produced from Mn ore and limestone, by mixing, heating and crushing


Ilmenite ore (used)
150 µm


Iron ore
300 µm

The <u>oxygen carrier</u> is the blood of CLC

Metal oxide particles of size 0.1-0.3 mm.

Operational temperature in CLC is typically 850 – 1100°C

Manganese, iron, copper, nickel and ***combined* oxides*** have been successfully used in chemical-looping pilot operation.

Low-cost natural ores, e.g. ilmenite, manganese and iron ores well suited for solid fuels also successfully used in operation.

Highly performing manufactured materials are suitable for ash-free gaseous fuels,

e.g. calcium manganate ($CaMnO_3$)

- Full gas conversion
- Long lifetime
- From low cost raw materials

Chalmers' research in CLC

>500 oxygen carriers tested in the lab

>70 oxygen carriers in pilot operation (>4200 h)

Operation world-wide in 49 pilots
222 publications, ⅓ solid fuels

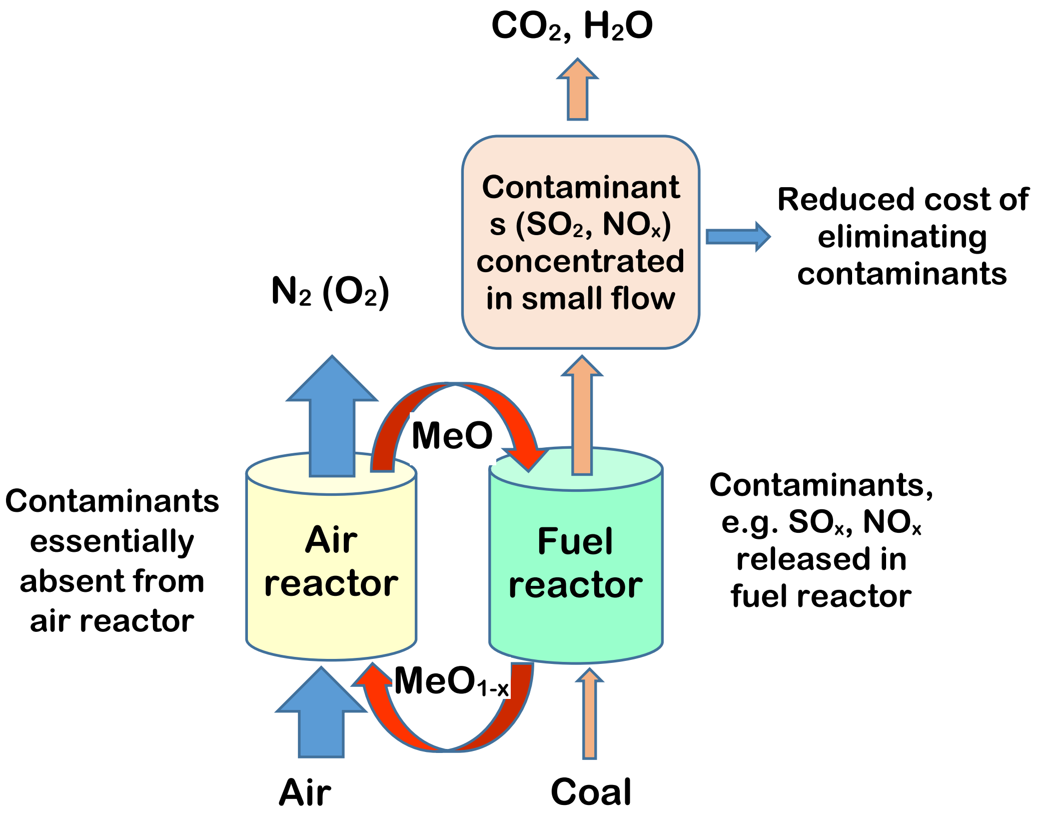
Type	Oxygen carrier	Time of operation	Percent
Manufactured	NiO	**3291**	**28%**
	CuO	**1455**	**12%**
	Mn_3O_4	**91**	**1%**
	Fe_2O_3	**1842**	**16%**
	CoO	**178**	**2%**
	Combined	**1480**	**13%**
Natural ore or waste material	Fe ore	**1075**	**9%**
	Ilmenite	**1524**	**13%**
	Mn ore	**735**	**6%**
	$CaSO_4$	**75**	**1%**
Total manufactured		**8337**	**71%**
Total natural/waste		**3409**	**29%**
Total		**11746**	**100%**

Potential applications of CLC technology

- Coal combustion
- Biomass/waste combustion (negative emissions)
- Steam-Methane Reforming with Chemical-Looping Combustion (SMR-CLC)

Chemical-looping combustion of coal

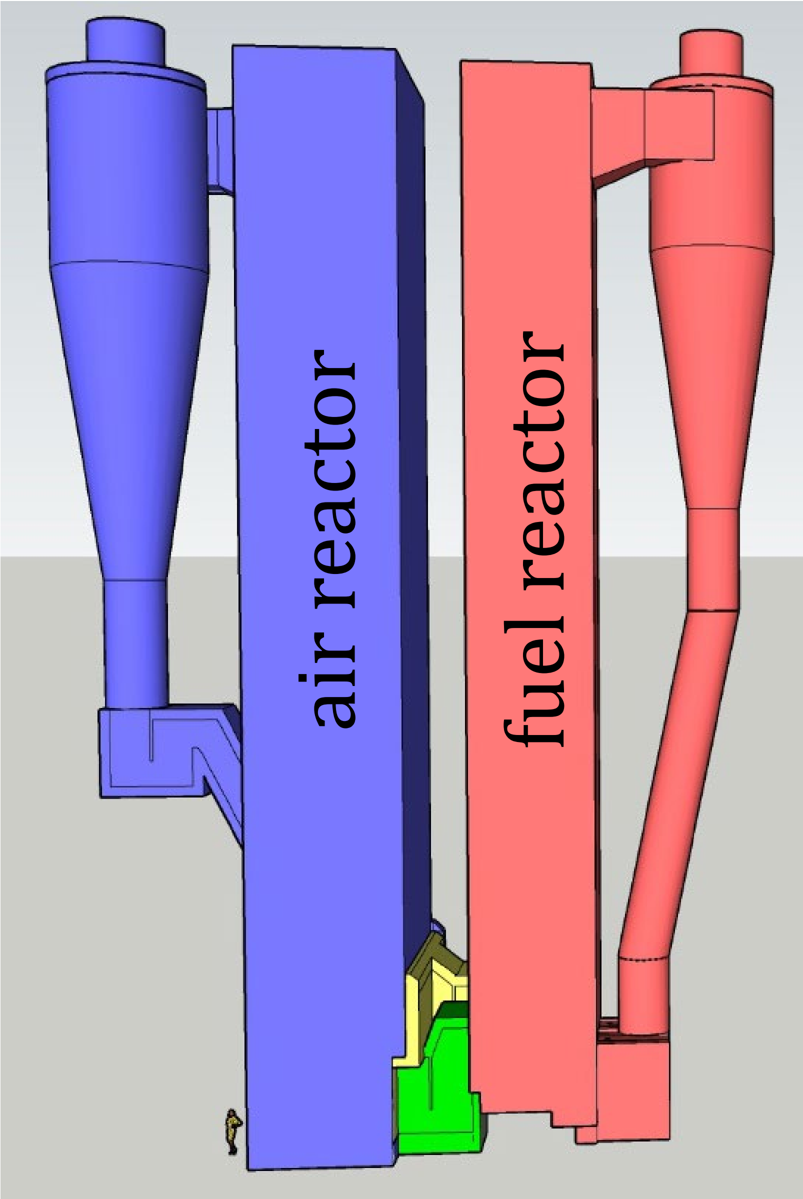
- high similarity to normal circulating fluidized bed combustion
- small added cost, low energy penalty
- pollutants concentrated in CO_2 could reduce costs of SO_x/NO_x reduction
- ***unique potential for dramatic reduction in CO_2 capture cost***
- large potential market

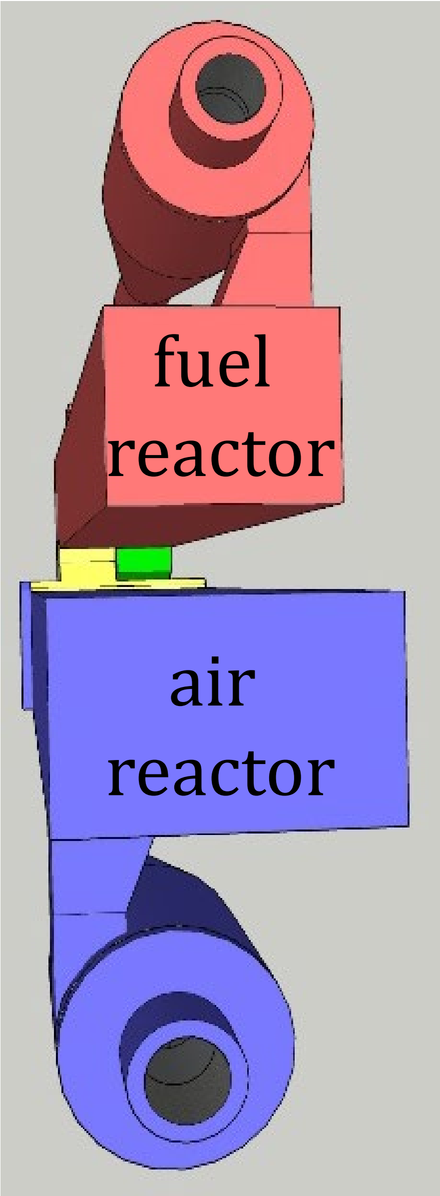


Chemical-looping combustion of biomass

- **Same advantages as with coal**
- important advantage with respect to alkalis
- negative emissions, future need for meeting exceeded carbon budgets

200 MW combined CLC-CFB boiler, 40 m high

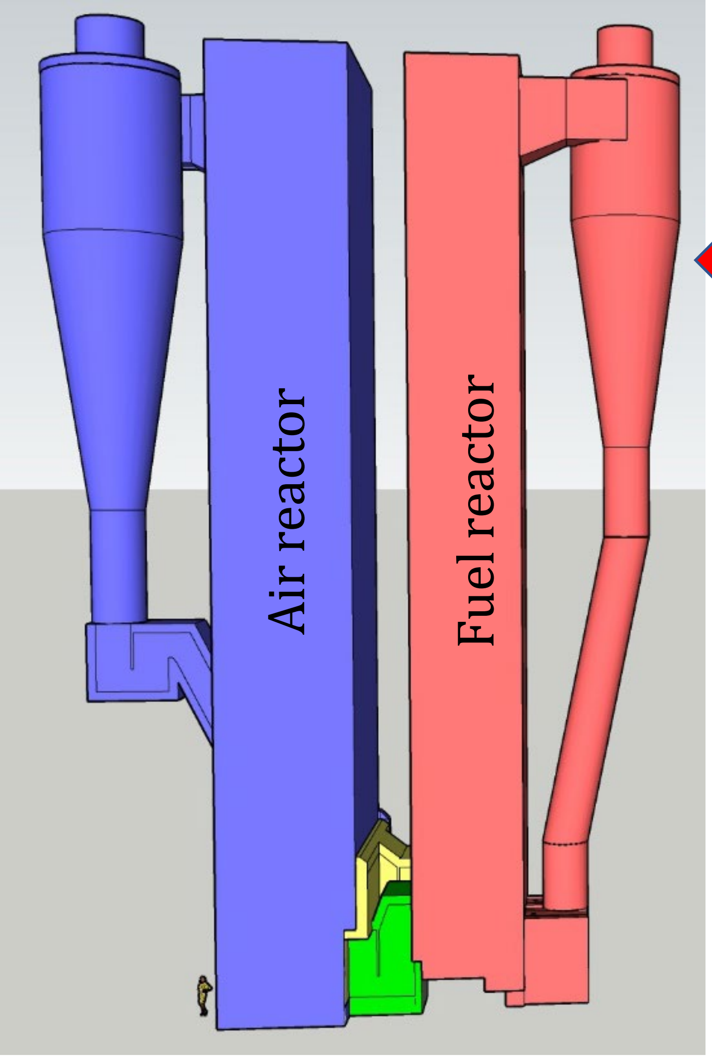


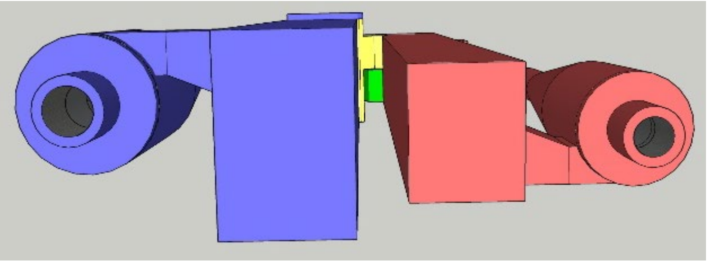


Air reactor can also be used as CFB boiler

Circulation based on collecting downfall along riser walls of air reactor

Lyngfelt, A., Pallarés, D., Linderholm, C., Lind, F., Thunman, H., and Leckner, B., Achieving Adequate Circulation in Chemical-Looping Combustion – Design Proposal for a 200 MW_{th} CLC Boiler, *Energy & Fuels* 36:17 (2022) 9588–9615





200 MW CLC-CFB, added cost of Fuel Reactor:

1500 m^2 insulated wall
at
2000 €/m^2

⇒ 1500 x 3000 = 3 M€

10% depreciation

⇒ **0.3 M€/year**

capture: 0.4 MtCO_2/year

cost of fuel reactor : $\frac{\mathbf{0.3\ M€/year}}{\mathbf{0.4\ MtCO_2/year}}$ = **0.75 €/t CO_2**

Cost of post-combustion CO_2 capture: 100 €/t CO_2

Costs, CLC of solid fuels, estimated at 16-26 €/tCO_2

big cost

Type of cost	estimation, €/tonne CO_2	range, €/tonne CO_2	Efficiency penalty, %
CO_2 compression	10	10	3
Oxy-polishing	6.5	4-9	0.5
Boiler cost	1	0.1-2.3	-
Oxygen carrier	2	1.3-4	-
Steam and hot CO_2 fluidization	0.8	0.8	0.8
Fuel grinding	0.2	0.2	0.1
Lower air ratio	-0.5	-0.5	-0.5
Total	20	15.9-25.8	3.9

small cost

[1]Lyngfelt, A., and Leckner, B., A 1000 MW_{th} Boiler for Chemical-Looping Combustion of Solid Fuels - Discussion of Design and Costs, *Applied Energy* 157 (2015) 475-487

Blue hydrogen (=”CO_2-free” hydrogen)

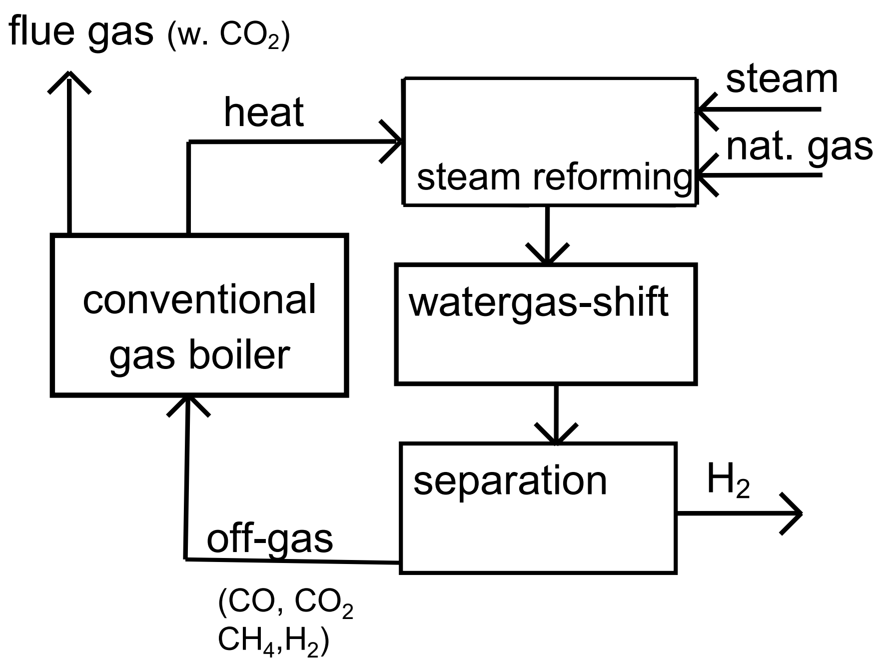
can be produced at low cost by combining

Steam Methane Reforming (SMR)
with
Chemical-Looping Combustion (CLC)

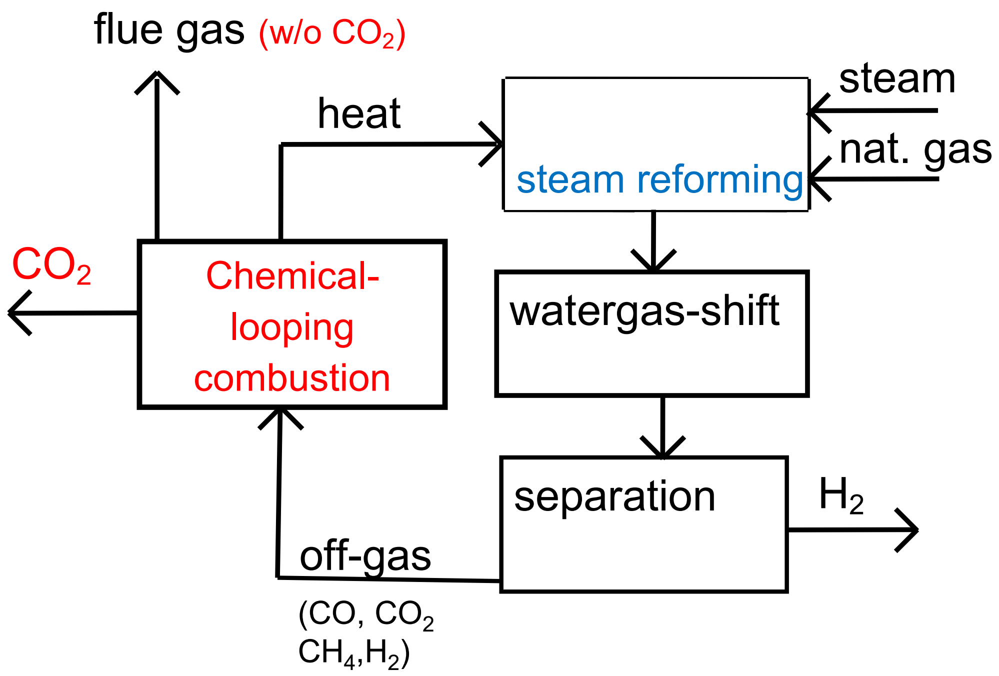
Natural gas is typically 90-95% methane

Steam Methane Reforming (SMR)
of natural gas
is the most common way of producing hydrogen,
but involves large emissions of CO_2

Normal steam methane reforming (SMR)



Steam reforming with CLC



Reforming:

CH_4 (methane) + H_2O + **heat** ⇒ CO_2 + CO + H_2O + H_2

Water gas shift:

CO + H_2O ⇒ CO_2 + H_2

Separation:

H_2(hydrogen) is removed from the gas mixture

Combustion:

Remaining gas + extra methane => **heat**

Carbon dioxide in a separate flow w/o separation

⇒ Natural gas converted to carbon-free fuel: i.e. hydrogen

Heat is transferred in a fluidized-bed heat exchanger (FBHE)

Summary: Why CLC-SMR?

Capture of CO_2 with no/small energy penalty

Negative energy penalty for process[1] (T outlet reduced from 1200 to 950°C)

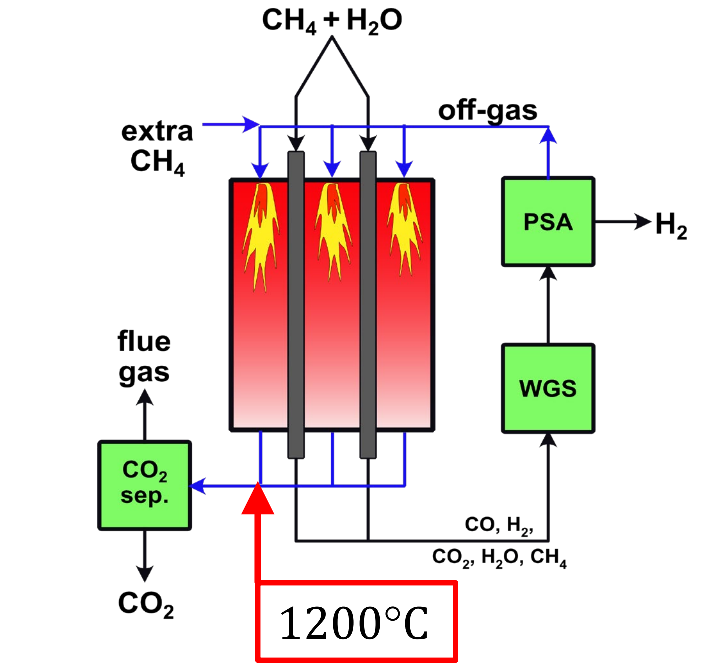
Capture of CO_2 with without high equipment/operational/energy cost for gas separation

More efficient heat transfer and more benign conditions

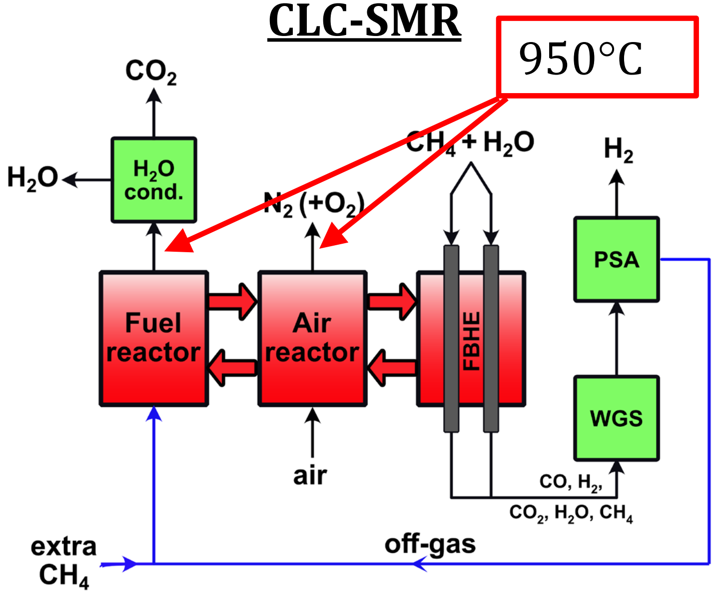
- smaller tube diameter possible in FBHEs (fluidized-bed heat exchangers)
- thus, shorter and thinner tubes (length decrease by factor 3 ?)[2]
- thus, less catalyst (amount decreased by factor of 3 ?)[2]
- thus, lower cost of reforming step

In total: Potential for transforming natural gas to CO_2-free H_2 with **<u>negative</u> energy penalty and <u>negative</u> cost penalty** for CO_2 capture. Gigantic potential future market.

Steam Methane Reforming (SMR)



CLC-SMR



1) Stenberg V, Spallina V, Mattisson T, Rydén M. Techno-economic analysis of H_2 production processes using fluidized bed heat exchangers with steam reforming – Part 2: Chemical-looping combustion. *International Journal of Hydrogen Energy* **46** (2021) 25355-25375

2) Pröll, T., and Lyngfelt, A., Steam Methane Reforming with Chemical-Looping Combustion – Scaling of Fluidized Bed-Heated Reformer Tubes, *Energy & Fuels* 36:17 (2022) 9502–9512

Chemical Looping combustion (CLC)

CLC boiler very similar to CFB boiler (=circulating fludized-bed boiler)

Highly concentrated CO_2 stream can be obtained at small added cost

Cost: 25-50% of competing technologies for solid fuels

- Eliminate/reduce emissions of SO_2 (coal)
- Eliminate/reduce emissions of NO_x (coal & biomass)
- Eliminate/reduce problems with alkali ash components (biomass)

Steam Methane Reforming with CLC

- Potential for lower cost than conventional SMR without CO_2 capture, i.e. ***negative*** capture cost

Oxygen carriers

Many different materials have been successfully used in pilot operation

Natural ores relevant for solid fuels

Manufactured CLOU materials could make sense for gas fuels, e.g. SMR-CLC

My favourites:

Ilmenite and manganese ore, possibly in combination, for solid fuels

Calcium manganate for gas fuels (SMR-CLC)

Thank you!