Materials for CHEMICAL-LOOPING COMBUSTION (CLC)

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CHALMERS

2nd ICEPE

Efficient Carbon Capture for Coal Power Plants
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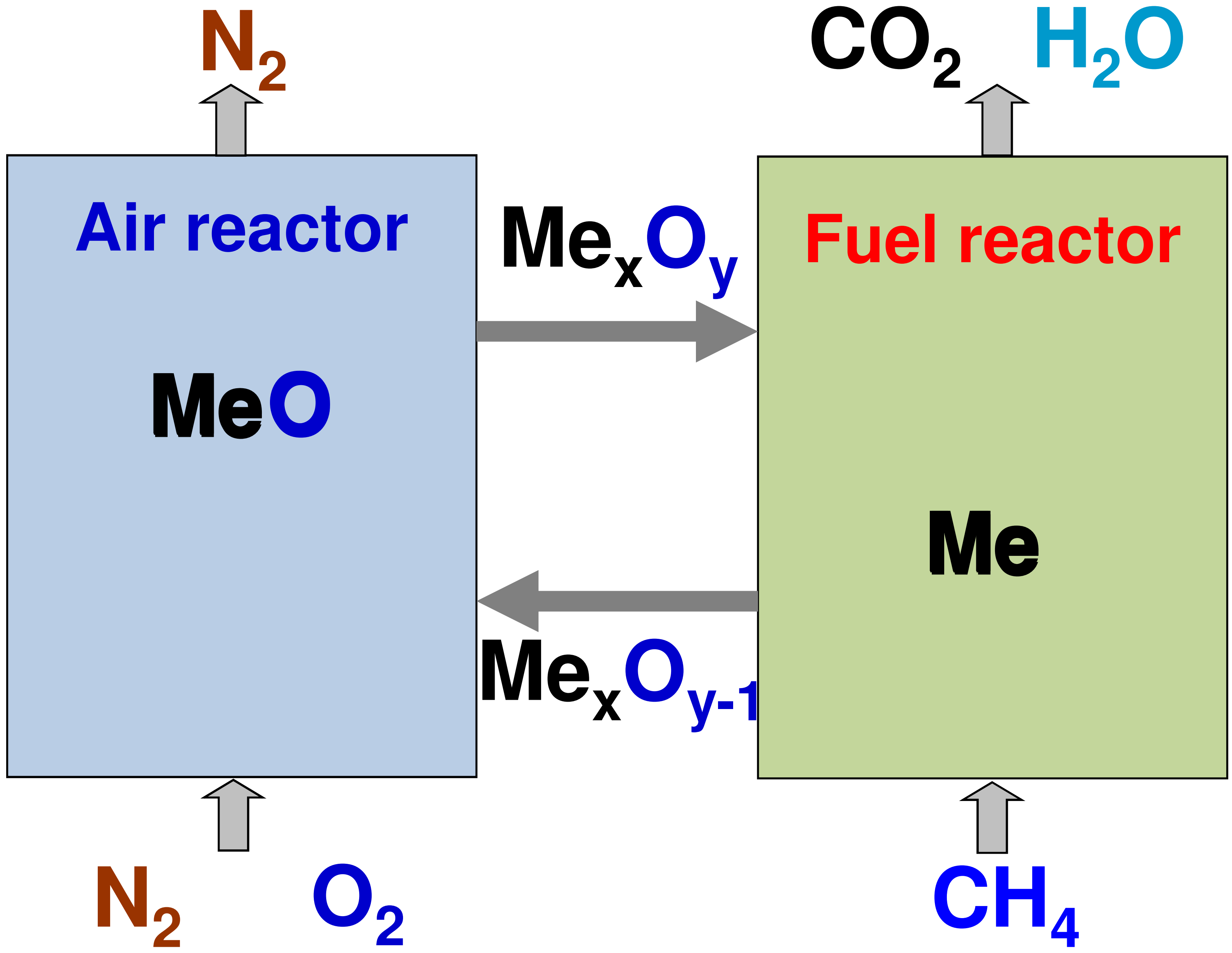
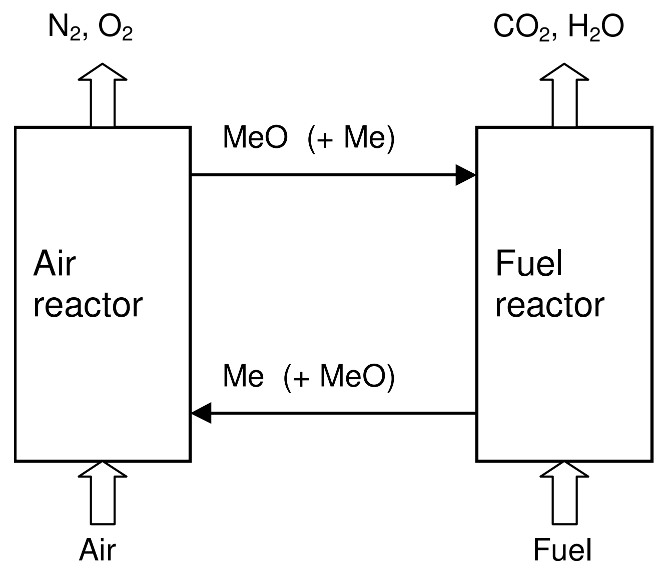
CO_2 capture

- **Main CO_2 capture processes (pre-, post-, oxy-) are all based on gas separation**
- **Gas separation inevitably needs energy**
- **From thermodynamics theoretical minimum energy needed can be derived**
- **Available gas separation processes are still far from this minimum, so there is room for improvement, but …**
- **Chemical-looping combustion has unique potential as no gas separation is needed**


N2
CO2 H2O
Air reactor
MexOy
Fuel reactor
MeO
Me
MexOy-1
N2 O2
CH4

Chemical-looping combustion (CLC)

- **Oxygen transferred from combustion air to fuel by metal oxide particles**



- **Inherent CO_2 capture:**
  - **fuel and combustion air never mixed**
  - **no active gas separation needed**
  - **large costs/energy penalties of gas separation avoided**

- **Potential for real breakthrough in costs of CO_2 capture**

CLC is a *new* principle of fuel conversion

Energy production from fuels

respiration	~2 000 000 000 BC
fire	~500 000 BC
fuel cell	1839
chemical-looping combustion	2003

CLC can be used for

- CO_2-free combustion of fossil fuels
- CO_2-negative combustion of biofuels (atmospheric CO_2 capture)
- Conversion of fossil fuels to CO_2-free fuels (below)

Chemical-looping steam reforming:

- Marriage between conventional steam reforming and chemical-looping combustion
- Converts natural gas to hydrogen and captured CO_2
- Provides hydrogen, a CO_2-free fuel, at 38 €/MWh
- 38 €/MWh less than world market price of crude oil, and appr. 1/3 of price of petrol.

Chemical-Looping Combustion (CLC) history

1954 patented in US for CO_2 production, forgotten

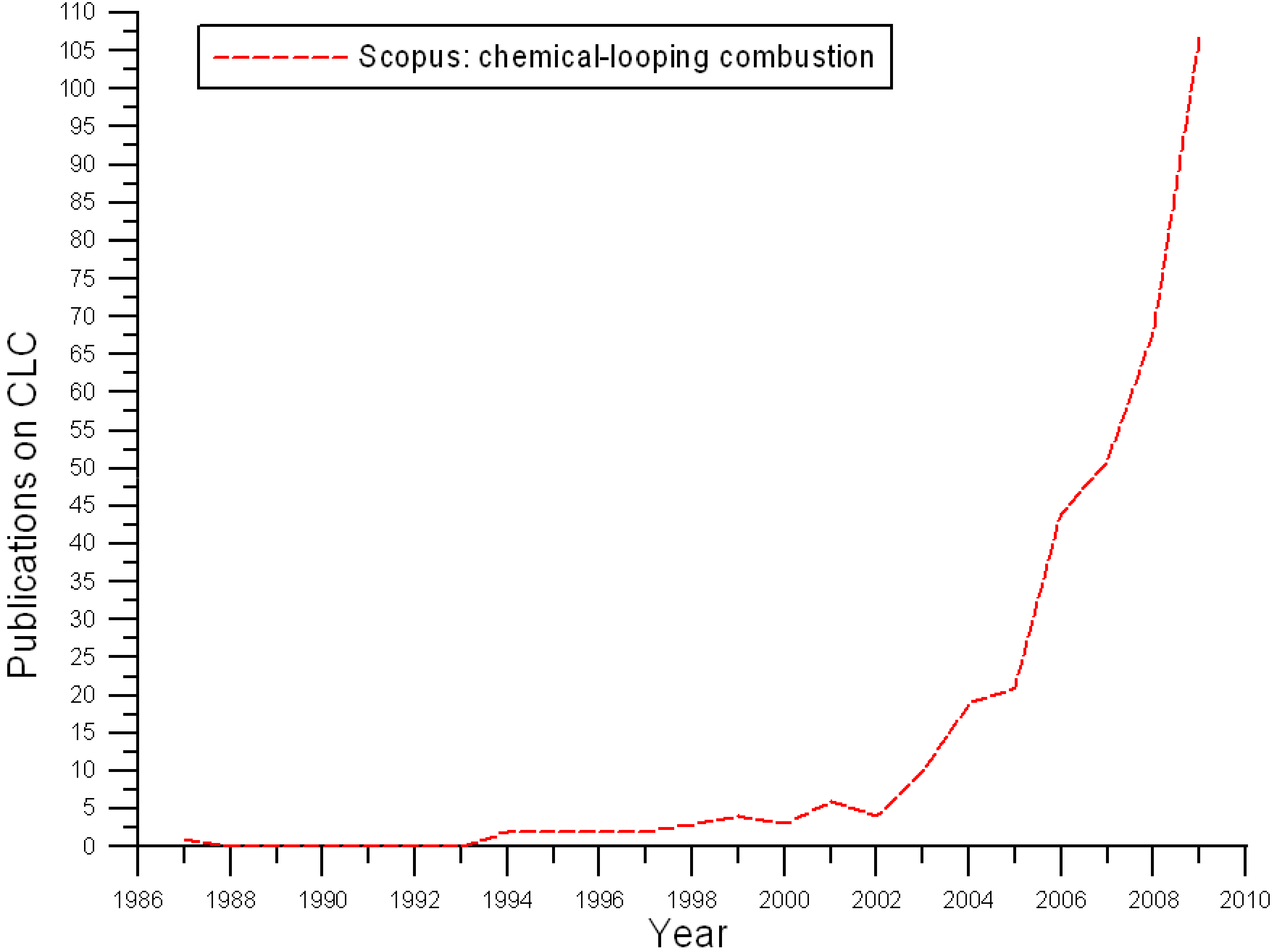
1987/1988/1994 Ishida in Japan introduces the name CLC / starts experimental research / proposes CLC to reduce CO_2 emissions

2003 first successful demonstration 100 h (Chalmers)

2006 first operation with solid fuels (Chalmers)

2011 >900 oxygen-carrier materials tested in lab

>4000 h of operational experience in 14 units worldwide (0.3-140 kW), 30 mtrls


Scopus: chemical-looping combustion
Publications on CLC
Year
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
1986
1988
1990
1992
1994
1996
1998
2000
2002
2004
2006
2008
2010

Oxygen carrier development.

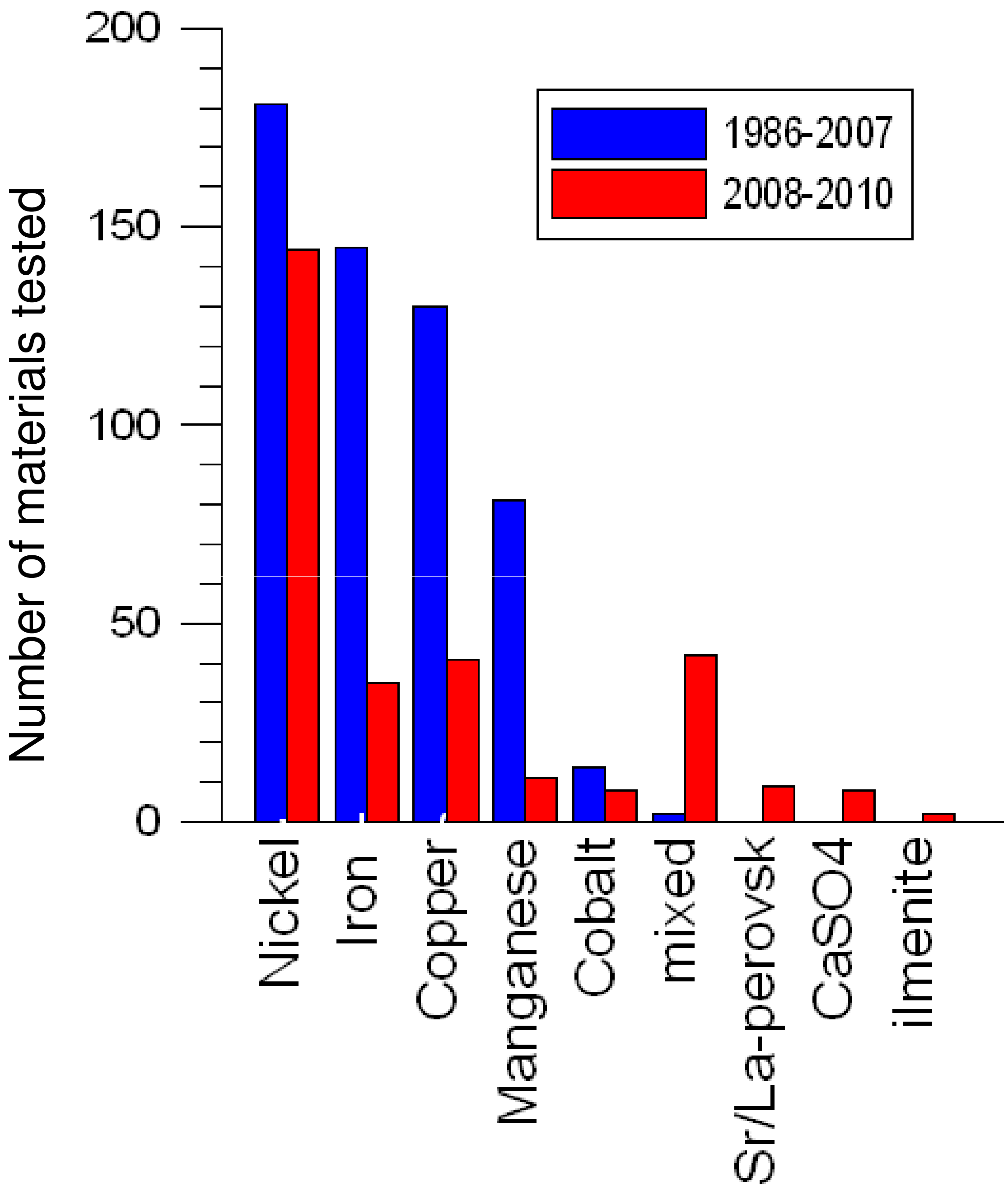
Mainly oxides of Nickel, Iron, Copper and Manganese (NiO, Fe_2O_3, CuO, Mn_2O_3)

Often supported on inert material.

Materials mostly tested in laboratory in cyclic operation (oxidizing-reducing cycles) in few cycles

Majority of materials tested in fixed beds (e.g. in TGA), but many hundred mtrls tesded under fluidized conditions

>30 materials tested in actual operation



Phase 1 1986-2007
>600 materials

Phase 2, 2008-2010
>300 materials

Reactivity

Methane (CH_4) and hydrocarbons

$NiO > CuO > Mn_2O_3 > Fe_2O_3$

in order of most reactive to least reactive

Hydrogen (H_2)

most materials very, very reactive

Carbon monoxide (CO)

most materials very reactive

Fe_2O_3 a bit lower though

COST

Cost Group	Type	Material	Indicative cost, €/ton
Low-cost	Waste mtrls	e.g iron oxides like oxide shell, red mud	0
	Ores	iron ore	50
	-“-	ilmenite (FeTiO3)	100
	-“-	manganese ore	300
Medium cost	manufactured mtrls	iron-based	>1000
	-“-	manganese based	>1000
Higher cost	-“-	copper-based	≥3000*
Expensive	-“-	nickel-based	≥20 000*
“Extreme cost”	freeze granulated	nickel-based	500 000

*Raw mtrl cost

Health, safety and environmental aspects

Nickel

- toxic and believed to be carcinogeneous
- safety measures needed in handling

Copper and Manganese oxides

- less toxic

Iron oxide

- edible ?

Pros and cons for the active oxides

	Fe	Mn	Cu	Ni
Reactivity w CH_4	- -	-	+	++
Cost	++	+	-	- -
Health				-
Thermodynamics				-[1]
Reaction with CH_4			+[2]	
Melting point			-[3]	

[1]maximum conversion 99-99.5%

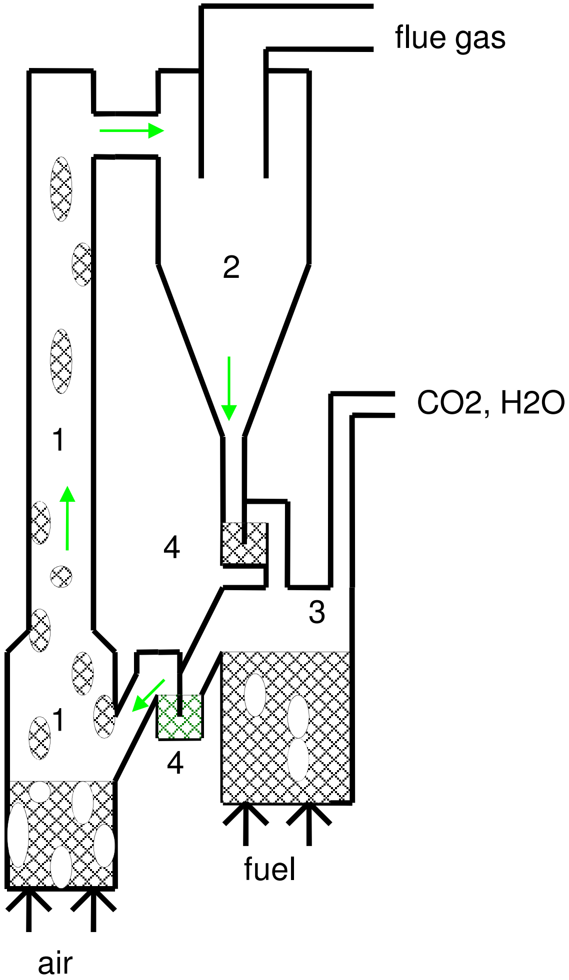
[2]exothermic reaction in fuel reactor

[3]melting point Cu: 1085 C

Operation in continuous chemical-looping combustors

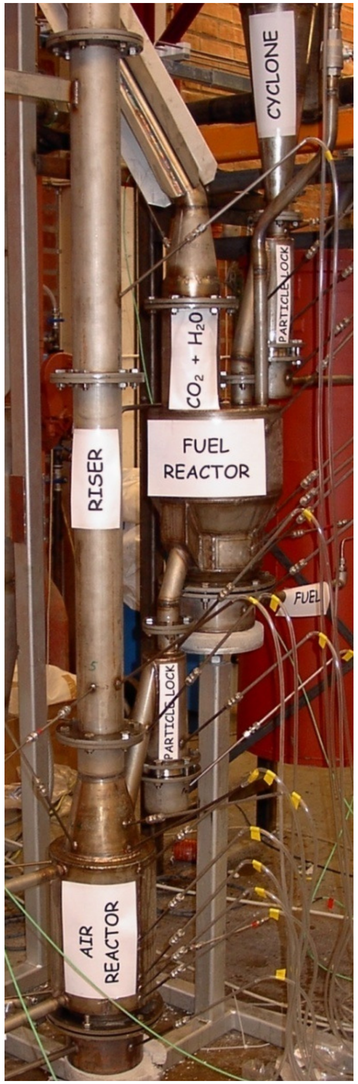
Location	Unit	Oxides tested	Time	Fuel	Year
Chalmers	10 kW	NiO, Fe_2O_3	1350	nat. gas	2004
KIER	50 kW	NiO, CoO	28	nat. gas	2004
CSIC	10 kW	CuO, NiO	140	nat. gas	2006
Chalmers	0.3 kW	NiO, Mn_3O_4, Fe_2O_3, ilmenite, $CaMnO_3$	730	nat. gas, syngas	2006
Chalmers	10 kW–SF	ilmenite	90	coal, petcoke	2008
CSIC	0.5 kW	CuO, NiO	660	nat. gas	2009
KAIST	1 kW	NiO + Fe_2O_3	?	CH_4	2009
Vienna UT	140 kW	ilmenite, NiO	390	nat. gas, CO, H_2	2009
Alstom	15 kW	NiO	100	nat. gas	2009
Nanjing	10 kW –SF	NiO, Fe_2O_3	230	coal, biom.	2009
KIER	50 kW	NiO, CoO	300	nat.gas, syngas	2010
Nanjing	1 kW - SF	Fe_2O_3 (ore)	10	coal	2010
IFP-Lyon	10 kW	NiO	?	CH_4	2010
Stuttgart	10 kW	ilmenite	?	syngas	2010

Chalmers 10 kW CLC, 2003

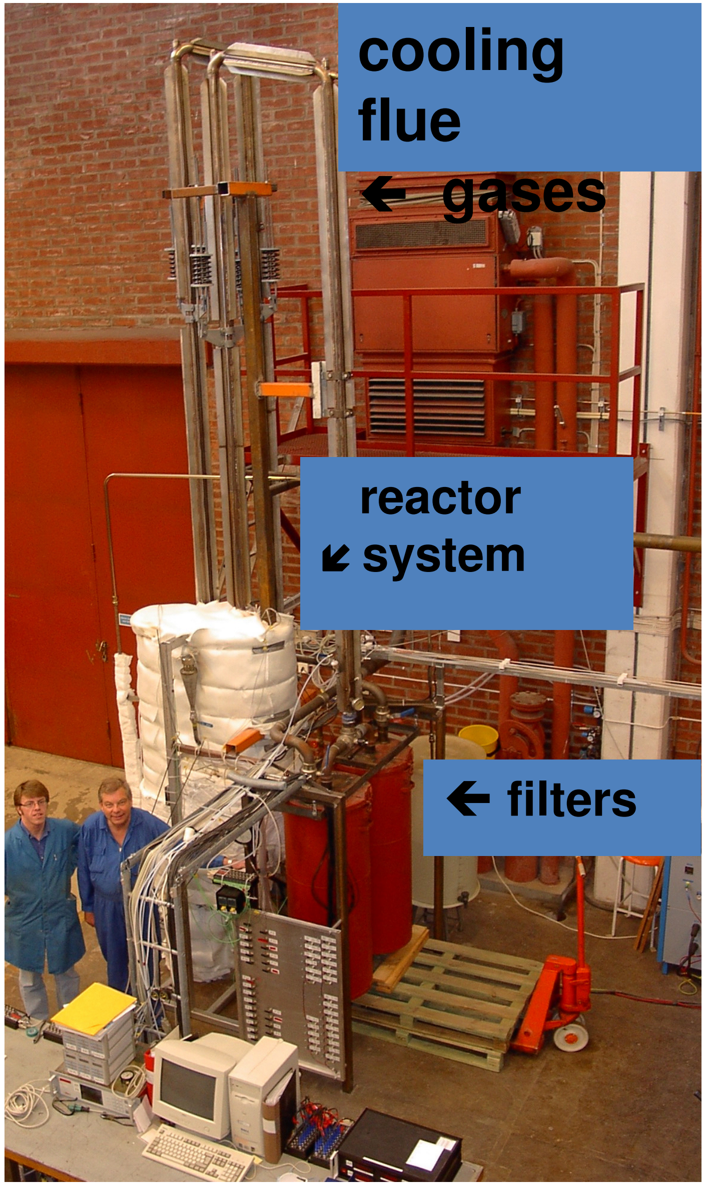


1 air reactor, 2 cyclone

3 fuel reactor, 4 loop seals



without insulation



CLC gaseous fuels

- 10 kW tests:
  - 100% capture of CO_2
  - 98% fuel conversion
  - one mtrl with >1000 h operational experience
  - long lifetime of material demonstrated
- best so far is nickel oxides
- work on-going with other oxygen carriers (better/cheaper)
- ready for scaling up to 1-10 MW_{th}

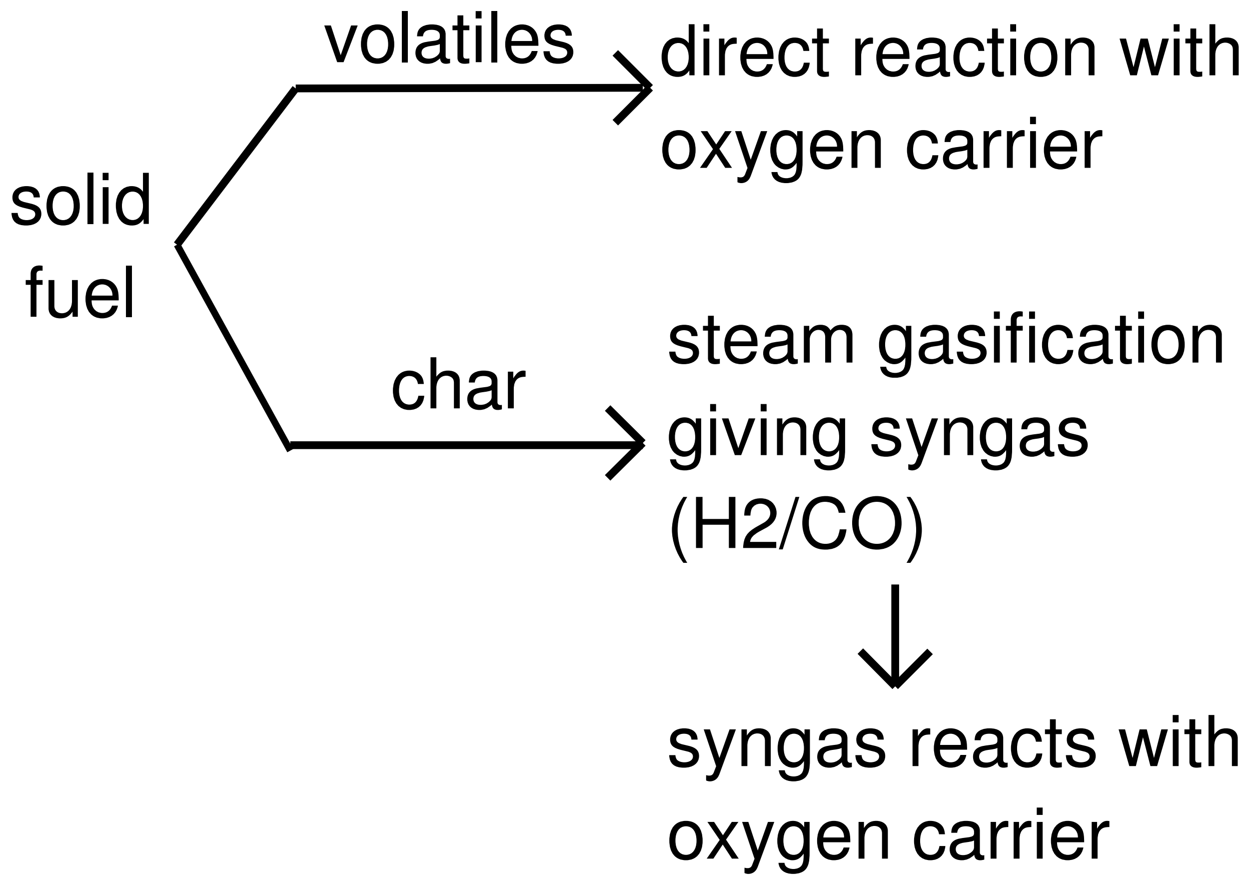
Solid fuel CLC

CLC technology very similar to Circulating Fluidized Bed Combustion, commonly used in power plants

Potential for a major break-through in cost and energy penalty :

- cost 10 €/ton CO_2 (reference 50 €/ton, ??)
- 3% loss in energy penalty (reference 10%)

CLC solid fuels



Solid fuel CLC, adaptations/challenges

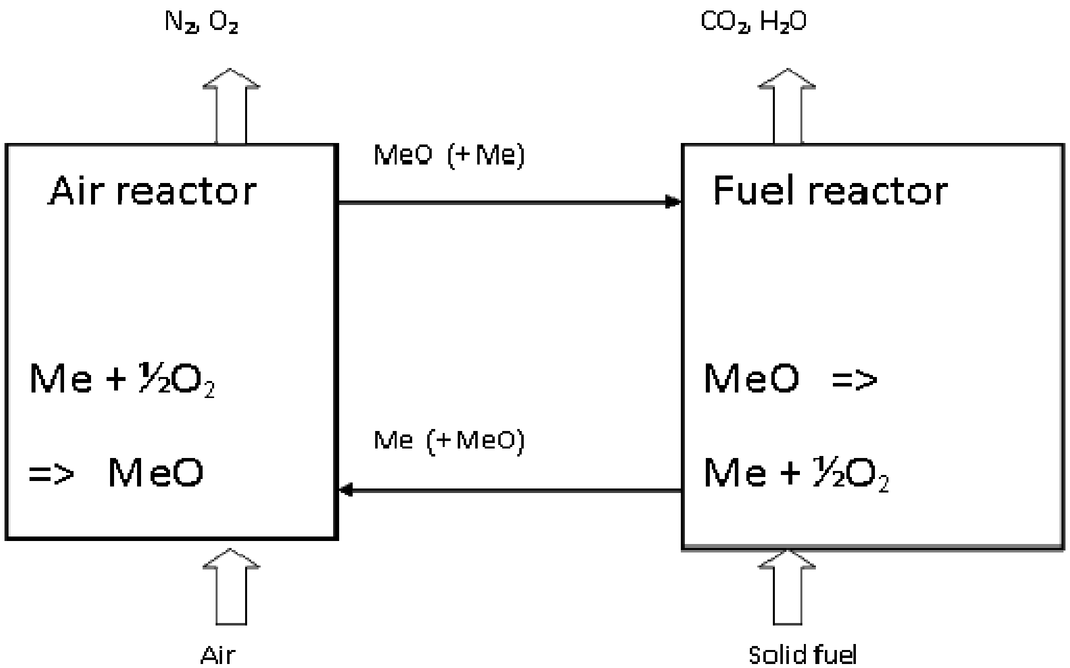
- cheap oxygen carriers because of fuel ash
  - e.g. ilmenite $FeTiO_3$ (natural mineral, 0.1 €/kg)
- bottom bed feeding of fuel (for conversion of volatiles)
- sufficient residence time of solids in fuel reactor (for char conversion)
- carbon stripper, converting/stripping char in solids flow to air reactor
- oxygen polishing, addition of oxygen to gas leaving fuel reactor to reach full gas conversion

Solid fuel CLC, alternate approach

Chemical-Looping with Oxygen Uncoupling

”CLOU”

uses oxygen carrier that releases gaseous oxygen in fuel reactor



CLOU

- oxygen carrier with suitable equilibrium partial pressures of O_2

- Example: $CuO \Leftrightarrow Cu_2O + ½O_2$
  - $p(O_2)_{equilibrium}$ = 2.5% at 925 C

- Copper oxide releases oxygen extremely fast. CuO decomposes to Cu_2O in <30 s. Char conversion rate may increase by 10-100 times, compared to steam gasification.

Chemical-looping with Oxygen Uncoupling (CLOU)

- In CLC fuel gases (CO, H_2, CH_4) react with oxygen carrier
- In CLOU, the oxygen carrier *decomposes* and releases oxygen which reacts directly with the fuel
- The trick: CLOU materials have an equilibrium partial pressure of O_2 around 1-5%. Thus, they take up oxygen in the Air Reactor and release oxygen in the Fuel Reactor, because the fuel keeps O_2 low
- Oxygen release is a great advantage with solid fuels
- …. but also with gaseous fuels because it facilitates reaching full gas conversion (in normal CLC very good contact between reacting gas and bed material is needed)

CLOU

Two types of oxygen carriers for CLOU	
full CLOU	”partial” CLOU
copper oxide materials	manganese oxide combined with iron, calcium, magnesium, silica
extremely fast release of large amounts of oxygen	slower release and smaller amounts of oxygen released… (release of oxygen and direct reaction with reducing gases in parallel)
• very rapid conversion of char • complete conversion of gas	• complete conversion of gas • increased conversion rate of char

Focus up to now

- **gaseous fuels with hydrocarbons:**
  - **expensive oxygen carriers with high methane reactivity (Ni)**
- **solid fuels:**
  - **low cost oxygen carriers with high syngas reactivity (ilmenite)**

Future development ?

- **gaseous fuels with hydrocarbons:**
  - **oxygen carriers that release oxygen (Cu or combined Mn oxides)**
- **solid fuels:**
  - **oxygen carriers that release oxygen (Cu or combined Mn oxides)**

Summary

- Major cost of CO_2 capture and storage is capture
- Capture cost CO_2 is caused by *gas separation* (fundamentally and technically well understood, no very fundamental break-throughs likely)
- CLC is a new principle of combustion, where *no gas separation* is needed, because air and fuel are not mixed
- CLC has major potential to reach real *breakthrough* in costs and energy penalty for CO_2 capture
- CLC can be used for combustion of gaseous, liquid and solid fuels – and to produce”CO_2-free” fuel, hydrogen

Summary continued

- Oxygen carrier is *key* to low costs and high performance
- Best material depends on fuel/process.
- Trade-off with respect to price, reactivity, estimated liftetime, health/environment.
  - Optimization to select best material will suffer from uncertainties.
  - Thus, best material cannot yet be selected.
  - We need a portfolio of material with different properties/cost
- CLOU mtrls coming next ?

THANK YOU !

>140 publications on CLC to be found on:

http://www.entek.chalmers.se/~anly/co2/co2publ.htm