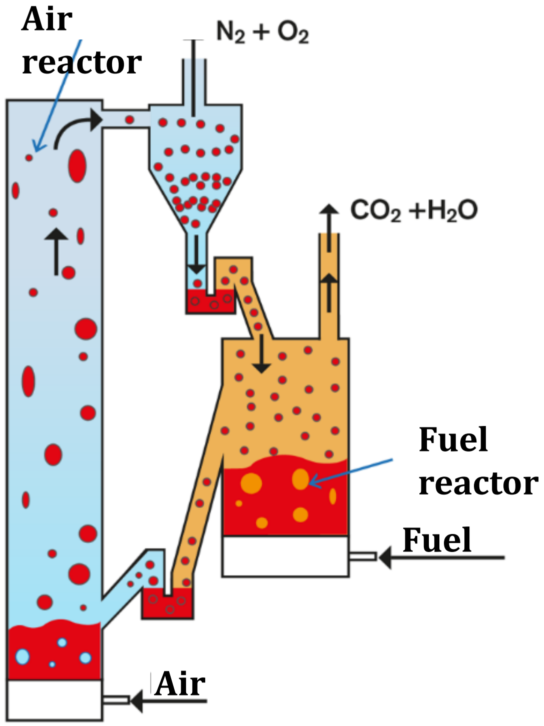
Chemical-Looping Combustion
-
CO_2 capture
at low cost and energy penalty



Anders Lyngfelt

Net-zero Emission Technologies
for Sustainable Development:
Challenges and Opportunities
N0ET – 2022
December 12-13
Dhanbad, India

CHALMERS

CONTENT

- Negative CO_2 emissions through Bio-Energy CCS
  - Principle
  - Need
  - Incentivizing

- Chemical-Looping Combustion (CLC)
  - Principles
  - Pilot experience
  - Oxygen carrier

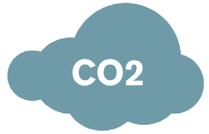
- CLC Applications
  - CLC of coal
  - CLC biomass
  - CLC for blue hydrogen

- Circulation

- Downstream treatment

Removal of CO_2 from the atmosphere
=
Negative Emissions

Bio-CCS

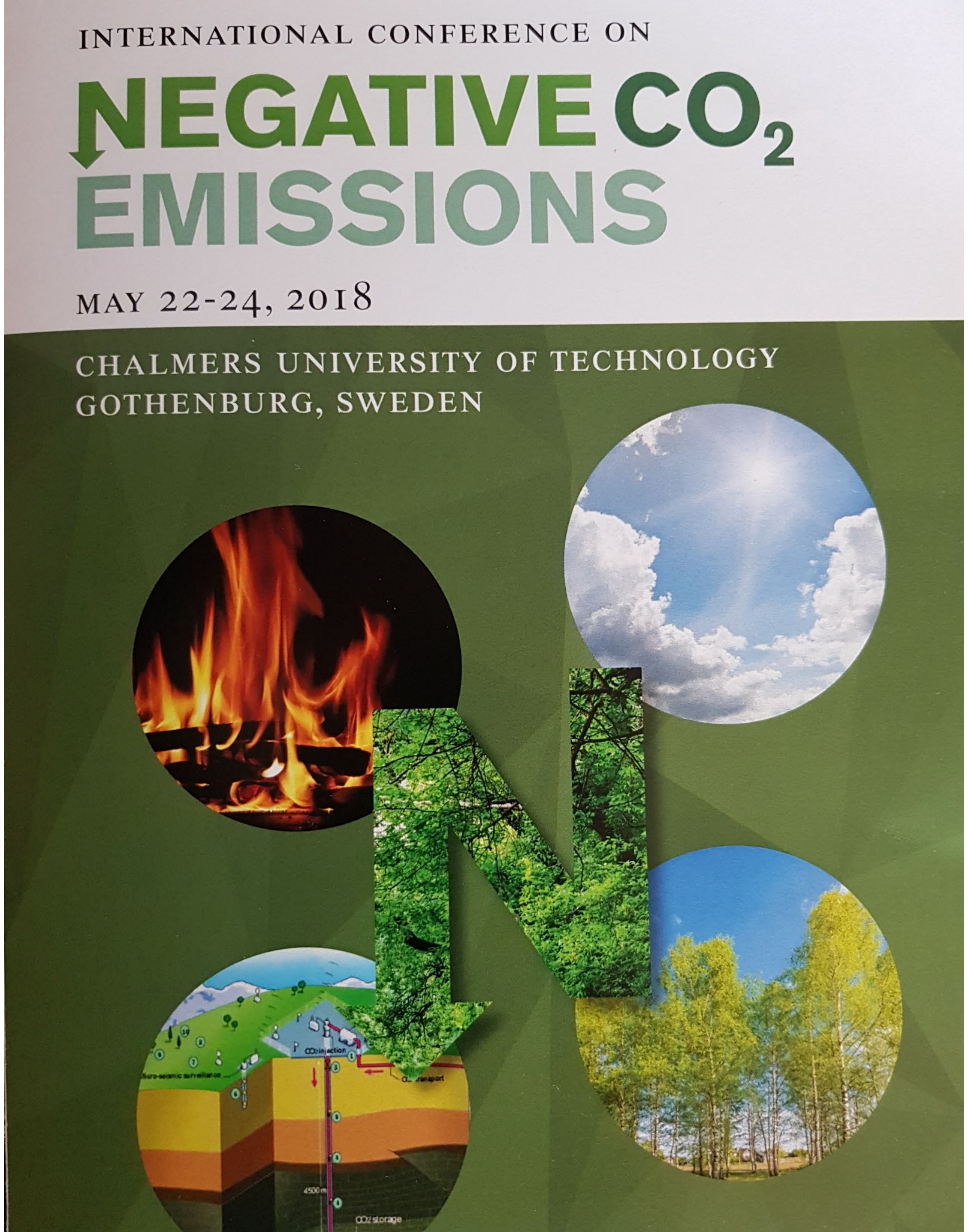


Growing trees/plants remove CO_2 from the atmosphere.

BUT, the CO_2 can be prevented from returning:

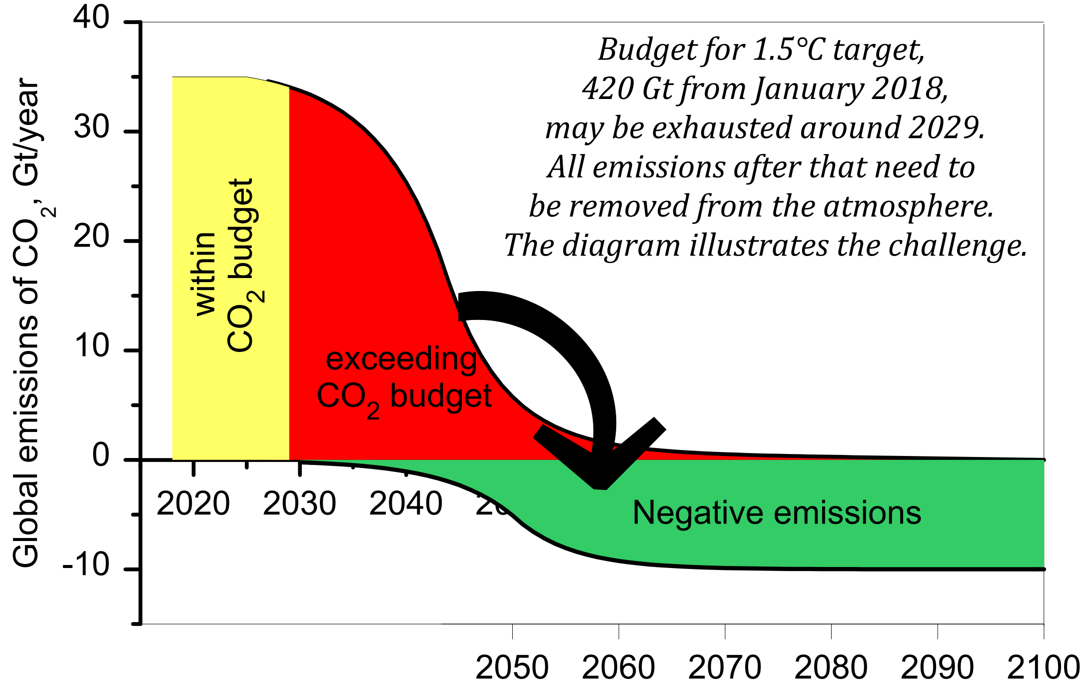
Capture and storage of CO_2 from combustion of biomass/biowaste

Bio-CCS (BECCS)
(BioEnergy Carbon Capture and Storage)

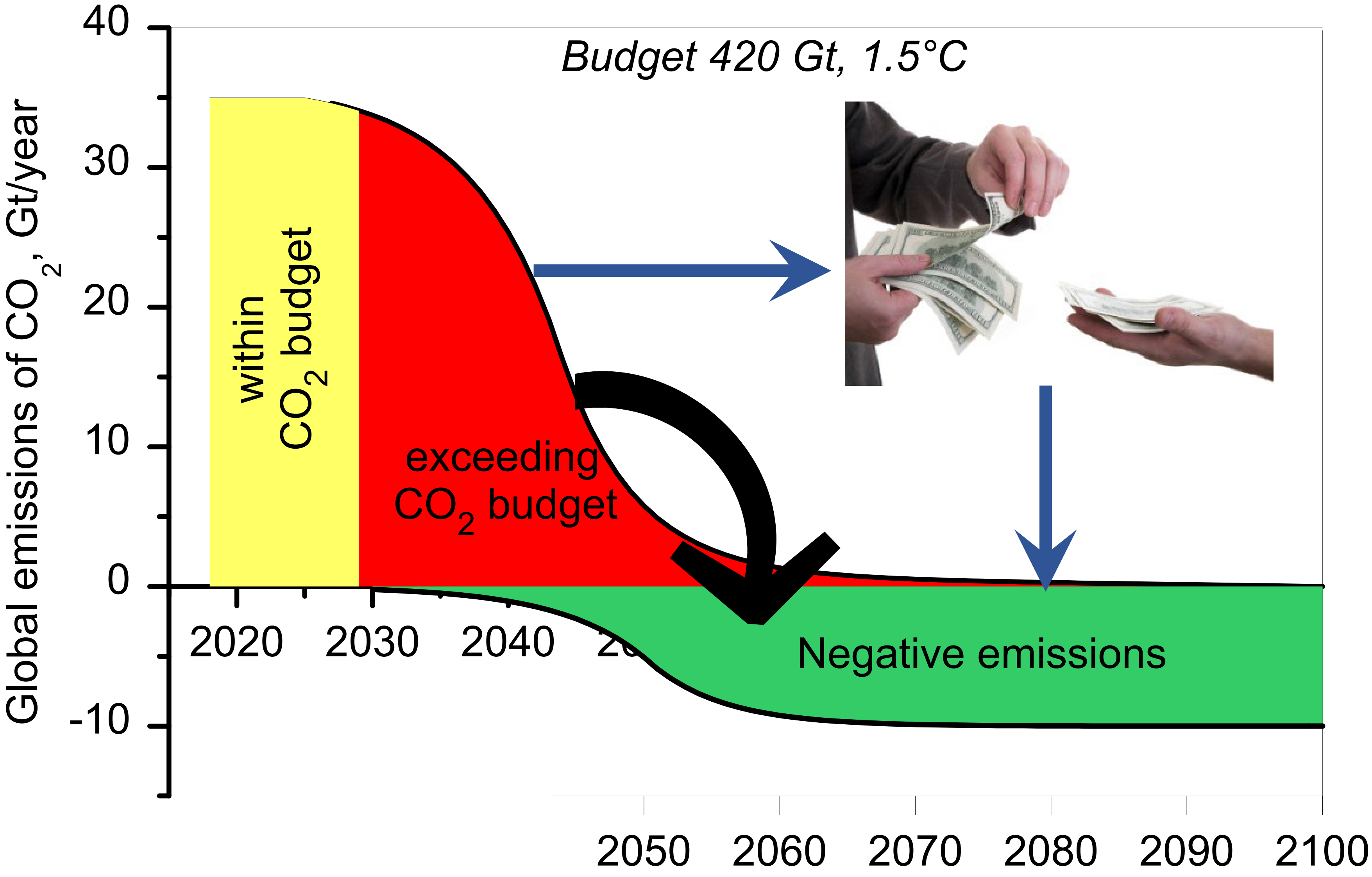

INTERNATIONAL CONFERENCE ON
NEGATIVE CO_2 EMISSIONS
MAY 22-24, 2018
CHALMERS UNIVERSITY OF TECHNOLOGY
GOTHENBURG, SWEDEN


2ND INTERNATIONAL CONFERENCE ON
NEGATIVE CO_2 EMISSIONS
JUNE 14-17, 2022

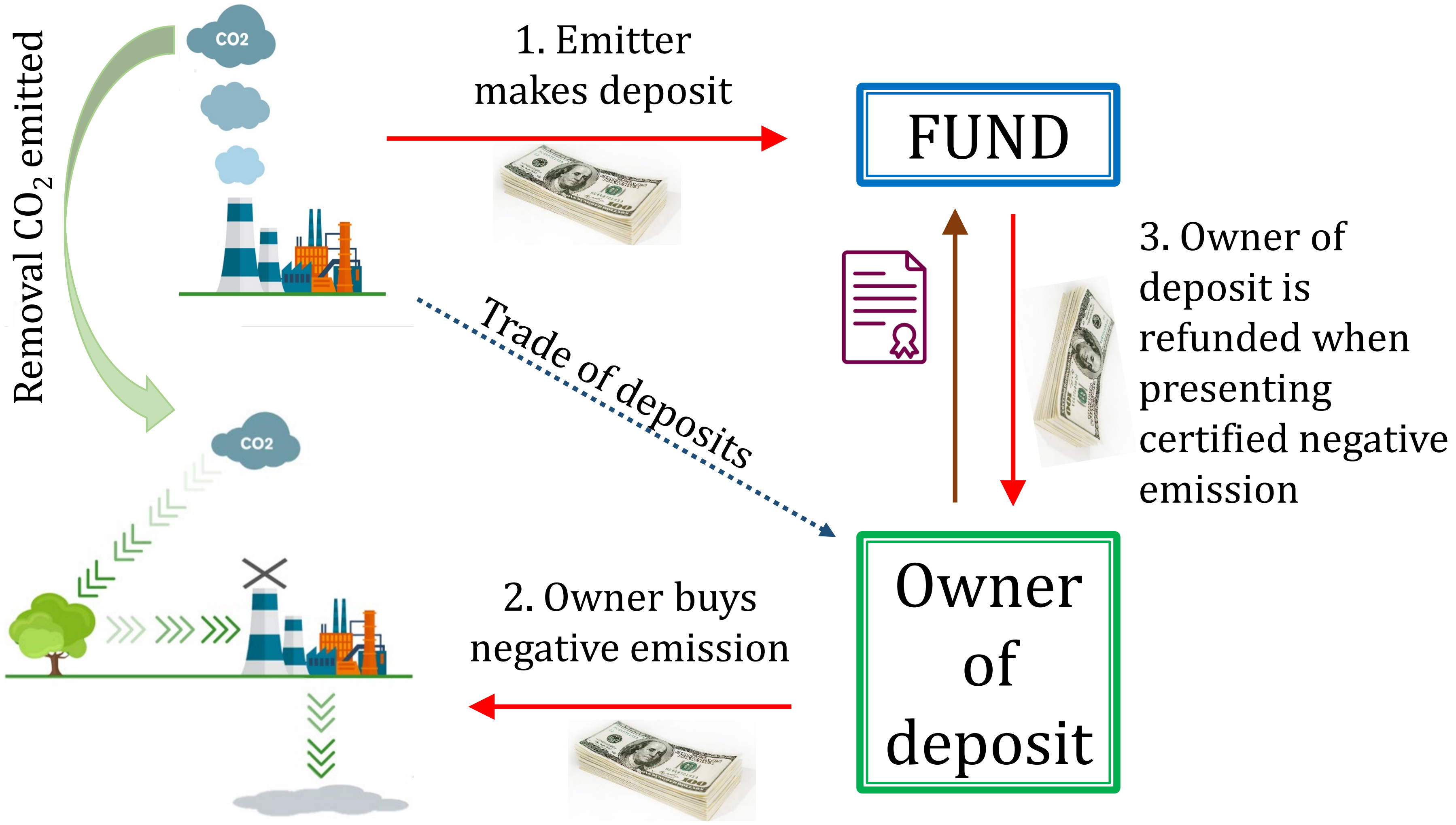
- Global carbon budget for +1.5°C likely spent around 2029
- Emission reductions cannot be made fast enough to meet the target
- To meet max 1.5°C, all CO_2 emissions after 2029 must be removed from the atmosphere.
- Enormous negative emissions needed to meet max 1.5°C,
- **No realistic mechanism for financing** of future negative emissions **in place**.



Proposal: Make emitters responsible for, i.e. pay for, removing emitted CO_2 from atmosphere



Atmospheric CO_2 Removal Deposits (ACORDs)



Lyngfelt, Anders, and Fridahl, Mathias, CO_2 Emitter Liability using Atmospheric CO_2 Removal Deposits (ACORDs) for Financing of Future Negative Emissions, *2nd International Conference on Negative CO_2 Emissions*, June 14-17, 2022, Göteborg, Sweden

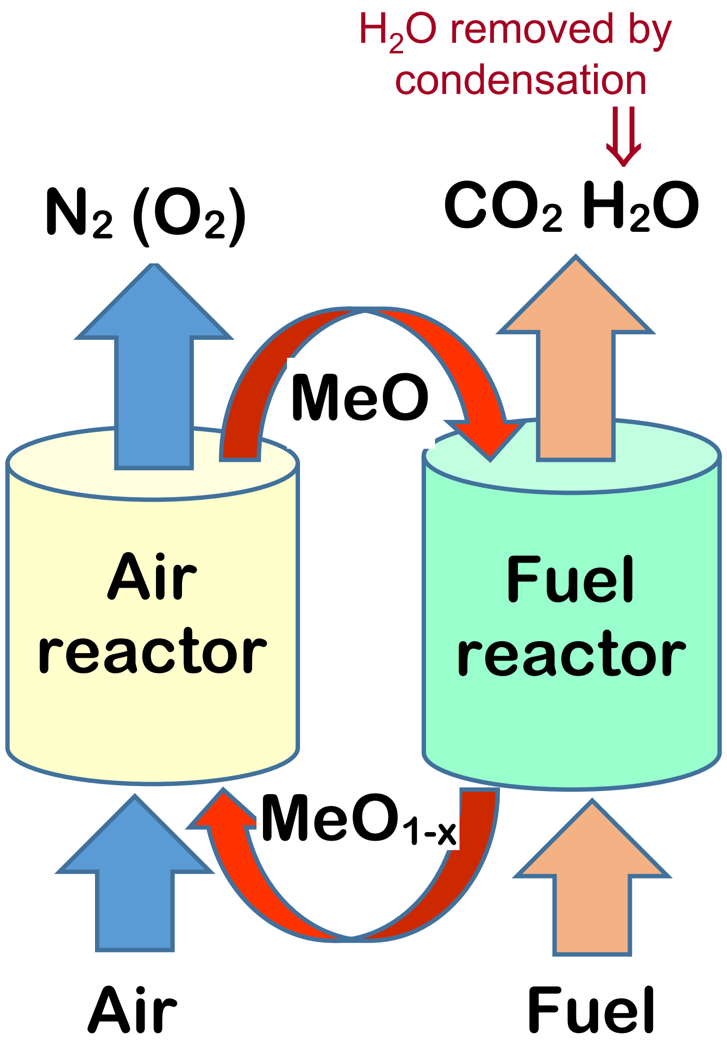
Chemical-Looping Combustion (CLC)

Oxygen is transferred from air to fuel by metal oxide particles

Inherent CO_2 capture:

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

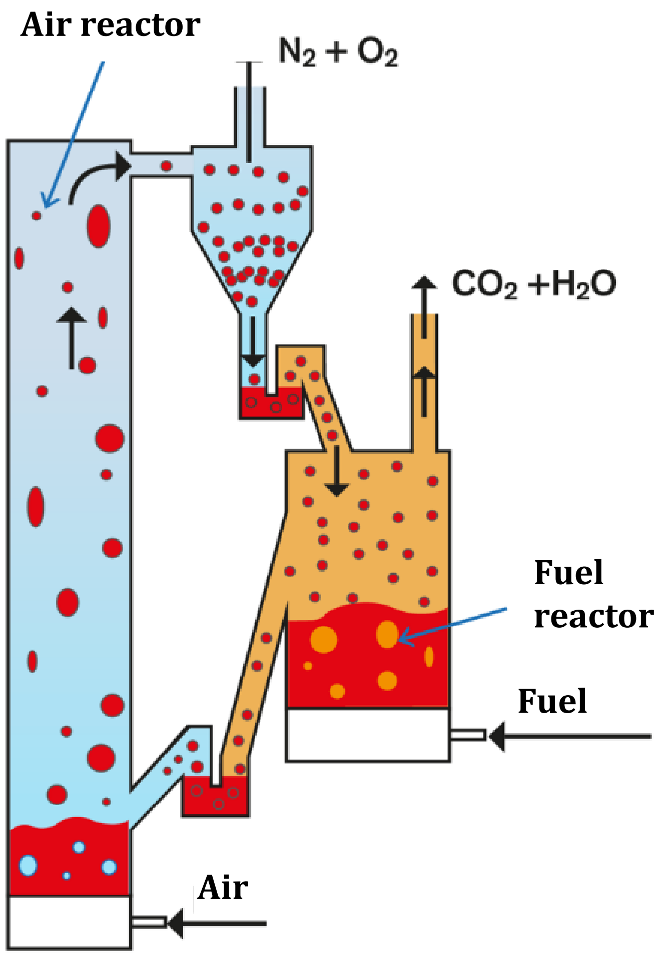
<u>Unique</u> potential for reducing costs of CO_2 capture!



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 ?

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

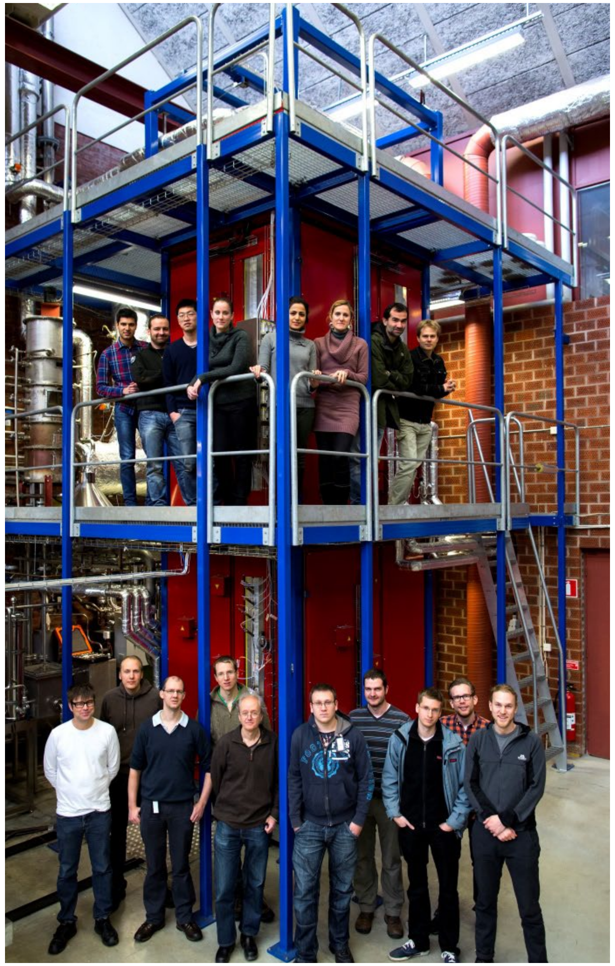
Yes, it works!!

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 cornerstone of CLC, analogous to the red blood cells transferring oxygen in the body

The oxygen carrier is made up of metal oxide particles of size 0.1-0.3 mm.

Operational temperature in CLC is typically 900 – 1000°C

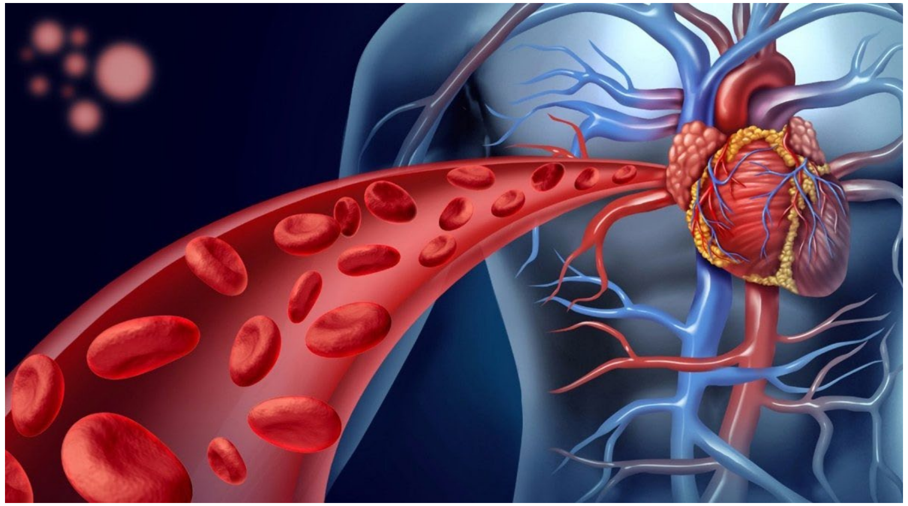
Oxides based on ***nickel, copper, iron and manganese*** have been successfully used in chemical-looping pilot operation.

Many combined oxides have also been used, e.g. manganese + calcium/iron/magnesium/silicon, and iron + titanium (ilmenite)

Both manufactured materials and low-cost materials, such as manganese ore, iron ore and ilmenite ore have been used.

Natural ores are well suited for ash-containing solid fuels, such as coal and biomass

Highly performing manufactured, such as calcium manganate, are suitable for ash-free gaseous fuels



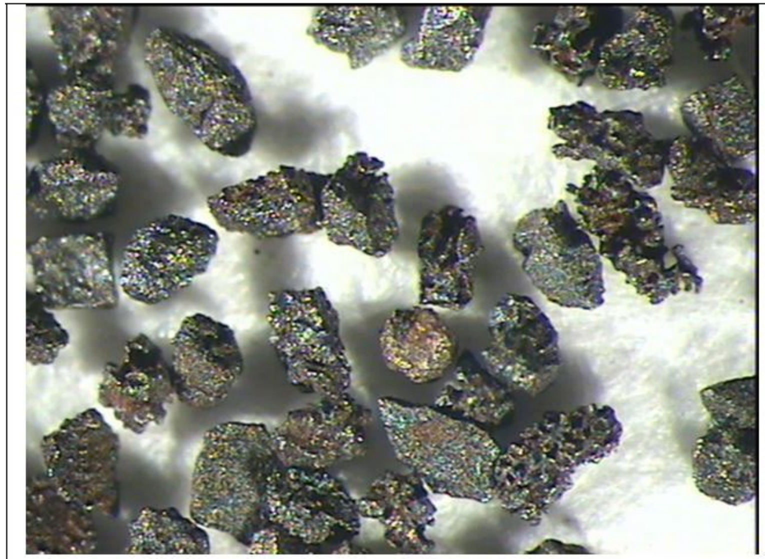


Figure 17 b. Used Mangagran particles, from AR. 180-212 μm.

Oxygen carriers continued

>12 000 h of chemical-looping operation in smaller pilots:

- a significant number of materials that work well
- manufactured materials with high, even complete conversion
- low-cost natural minerals/industrial by-products
- sufficient reactivity and lifetime has been shown by a number of materials

>20 000 h of Oxygen Carrier Aided Combustion (OCAC) with ilmenite in CFB boilers, shows it can be used at industrial conditions

Lyngfelt, A., Chemical-Looping Combustion – Status and Development Challenges, Energy & Fuels 32 (2020) 9077-9093

Lind F., Corcoran A., Andersson B.-Å., and Thunman H., 12,000 Hours of Operation with Oxygen-Carriers in Industrially Relevant Scale (75,000 kWth), *VGB Power TECH Journal*, **7** (2017)

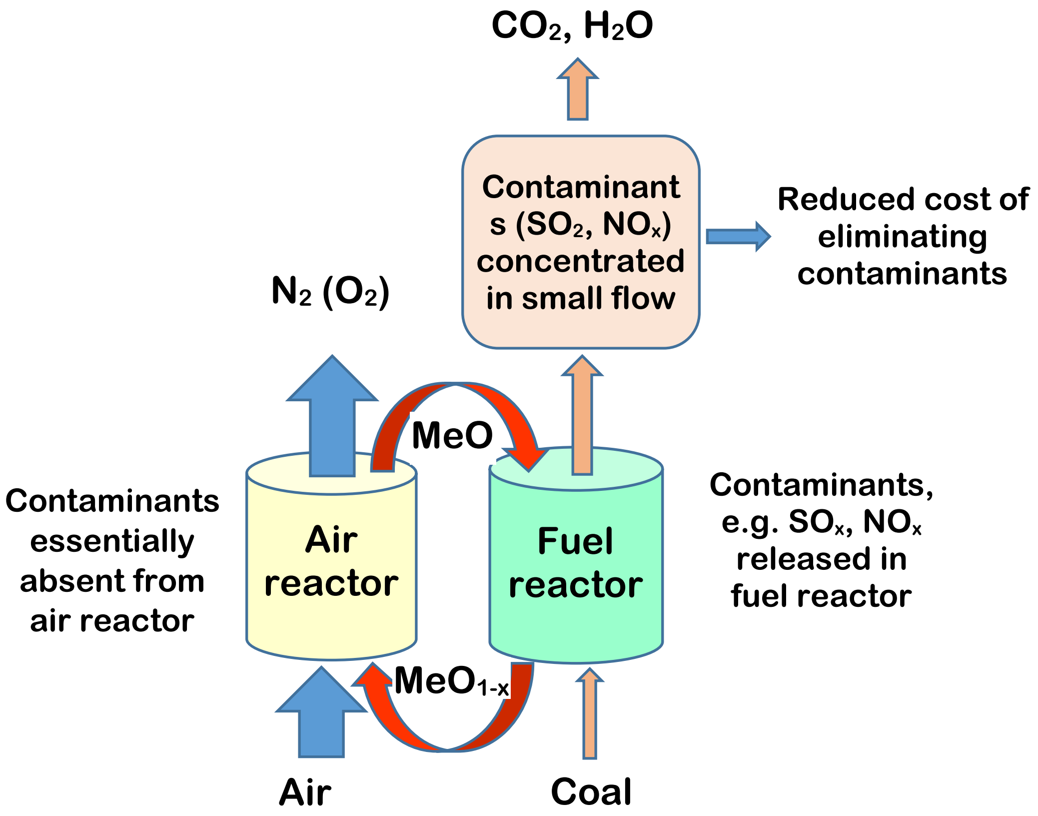
Moldenhauer, Patrick; Angelica Corcoran; Henrik Thunman and Fredrik Lind, A Scale-Up Project for Operating a 115 MWth Biomass-Fired CFB boiler with Oxygen Carriers as Bed Material, *5th International Conference on Chemical Looping,* Park City, Utah, 24-27 September 2018

Most important applications of CLC technology

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

Chemical-looping combustion of coal

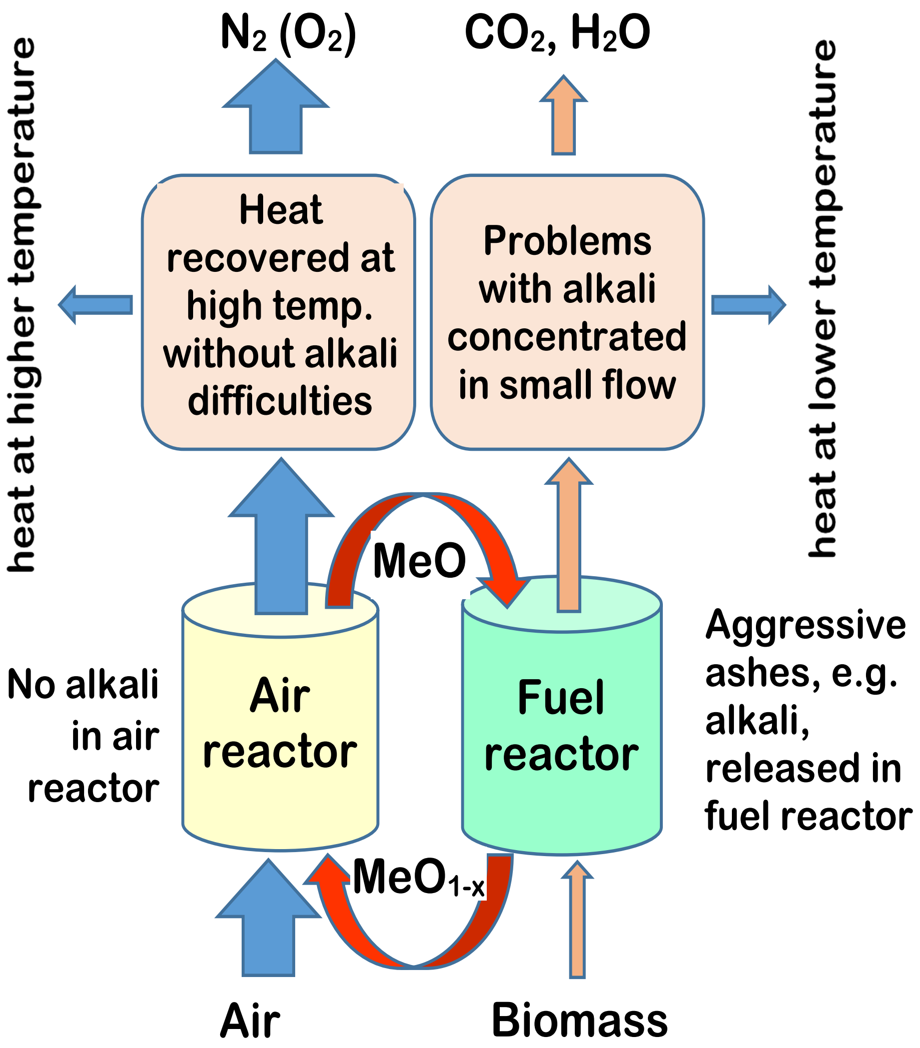
- high similarity to normal circulating fluidized bed technology
- small added cost, low energy penalty
- pollutants concentrated in CO_2 could reduce costs of SO_x/NO_x reduction
- ***unique potential for dramatic reduction in CO_2 capture cost***
- large potential market



Chemical looping combustion of biomass

- same advantages as in coal combustion above:
  - similarity to normal circulating fluidized bed technology
  - small added cost, low energy penalty
  - concentration of pollutants in CO_2
  - ***unique potential for dramatic reduction in CO_2 capture cost***
  - large potential market
- in addition potential advantage with respect to alkalis
- using biomass gives negative emissions
- to meet climate targets **gigantic negative emissions** are needed

Chemical-looping combustion of biomass



Alkali in biomass gives low ash-melting temperature together with silica (i.e. sand).

With ilmenite oxygen carrier ($FeTiO_3$) the alkali forms **non-sticky** titanates.

>20,000 h of OCAC (oxygen-carrier aided combustion) in full-scale CFBs with ilmenite

Long-term operation with ilmenite, 300 h, shows alkali penetrates to centre of particles, and only minor loss in reactivity

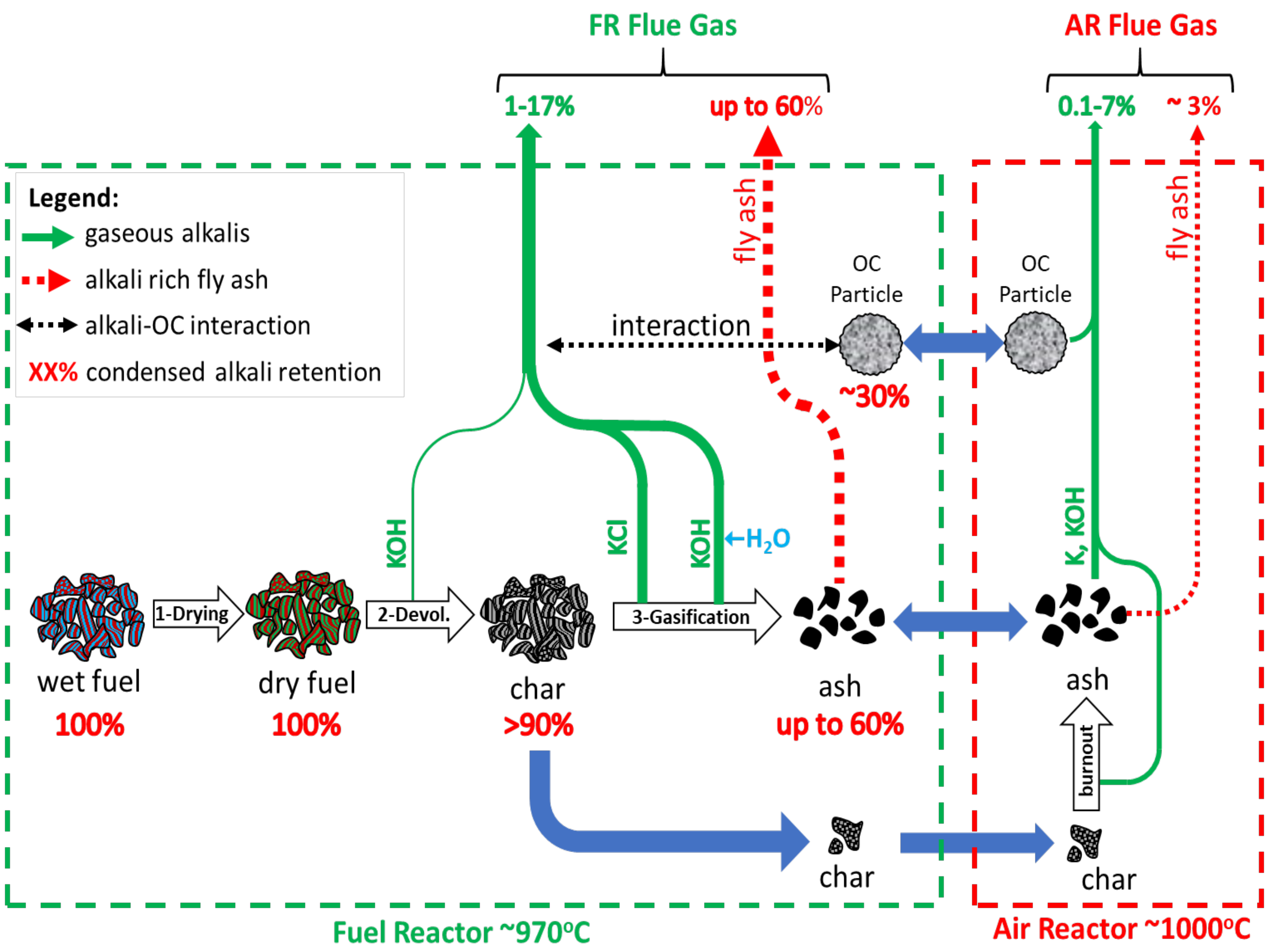
Only small part of alkali released in air reactor

Air reactor essentially free from chlorine

Could range of possible fuels be extended to more difficult fuels? (straw)

Studies of alkali flows in three CLC pilots found:

- majority of alkali retained in oxygen carrier
- majority of alkali in fly ash, from fuel reactor
- ***low fraction of alkali in air reactor outlet***
- ***air reactor will be essentially free of KCl***

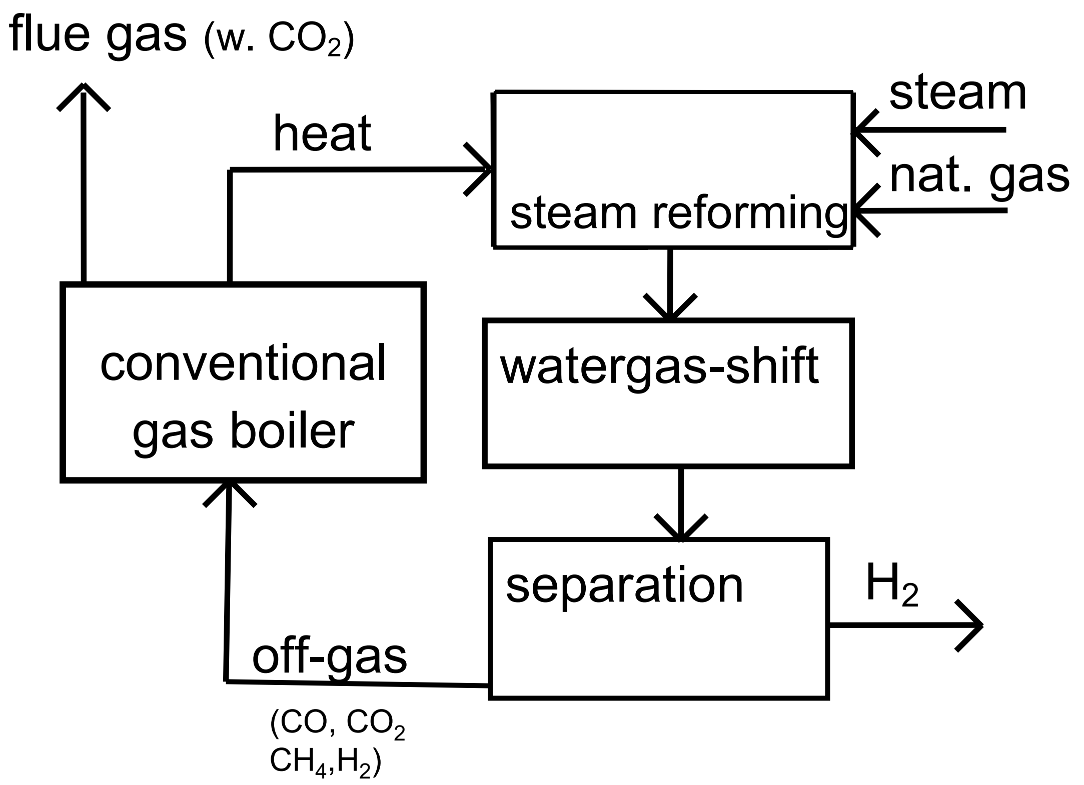


Ivan Gogolev, Amir H. Soleimani Salim, Daofeng Mei and Anders Lyngfelt, Effects of Temperature, Operation Mode, and Steam Concentration on Alkali Release in Chemical Looping Conversion of Biomass – Experimental Investigation in a 10 kWth Pilot, *Energy & Fuels,* 36:17 (2022) 9551–9570

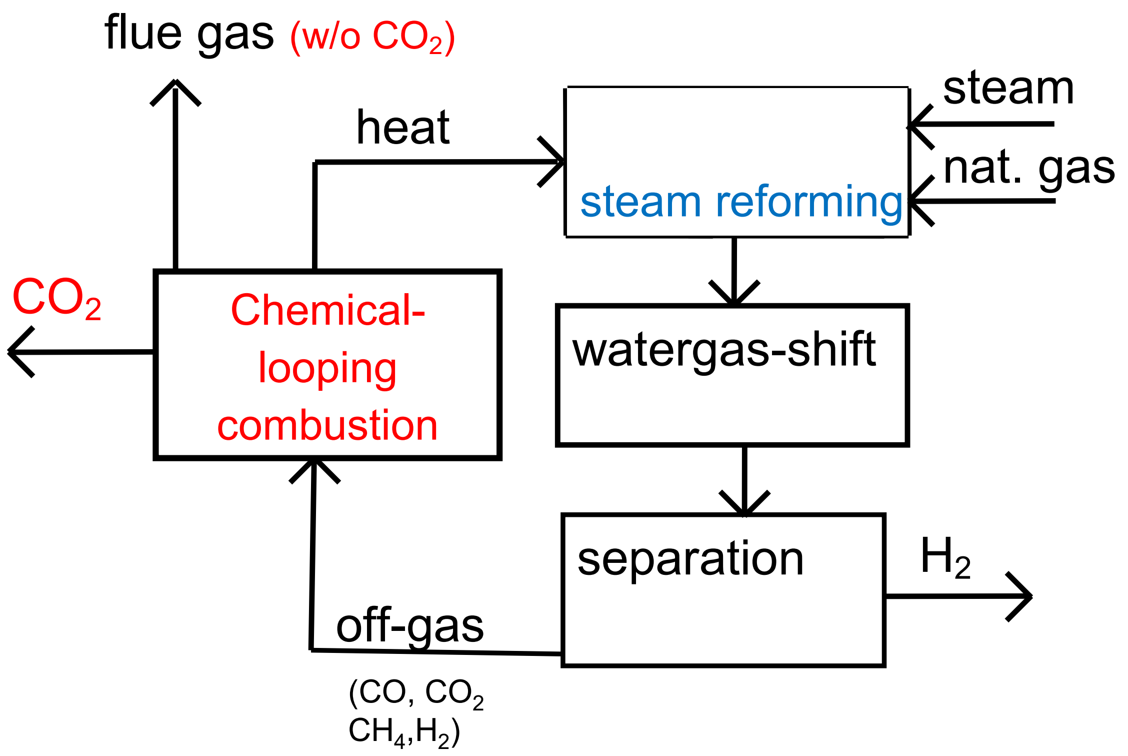
Ivan Gogolev, *The Release, Distribution, and Implications of Alkalis in Chemical Looping Combustion of Biomass*, PhD Thesis, Chalmers University of Technology, Göteborg, Sweden 2022

Blue hydrogen at low cost with CLC-SMR

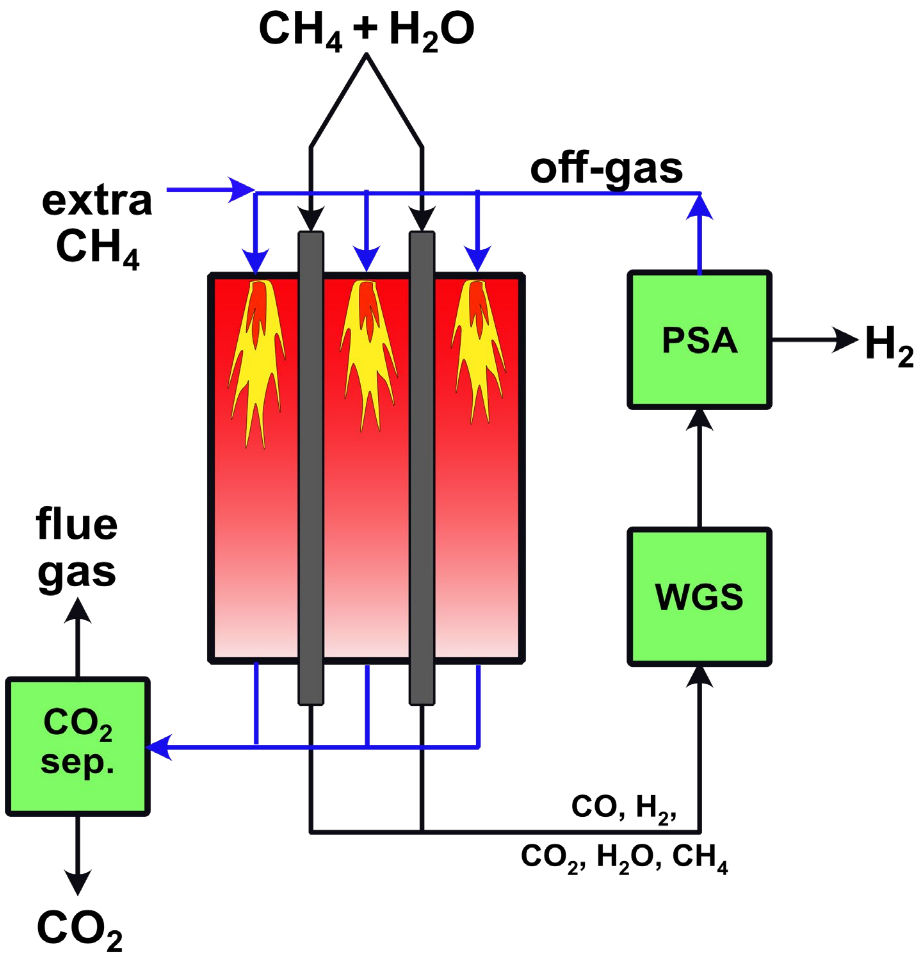
Steam methane reforming (SMR)



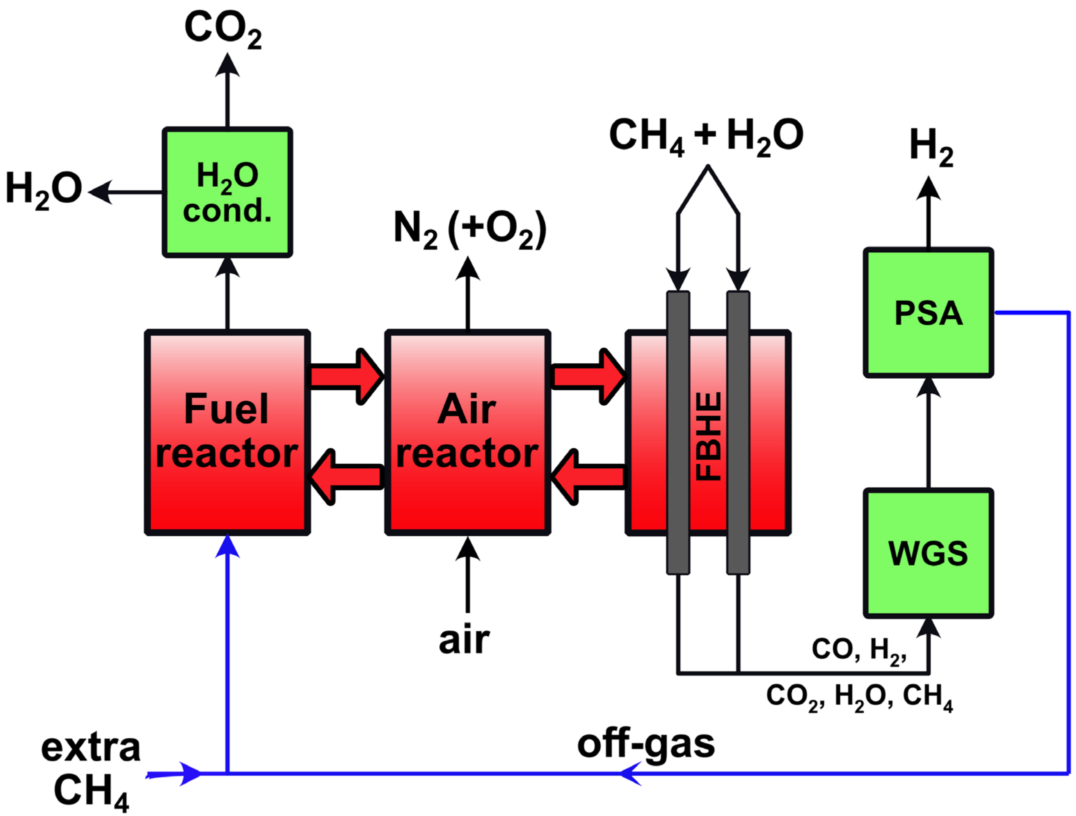
Steam reforming with CLC



Steam Methane Reforming (SMR)



Steam reforming with CLC



Why CLC-SMR?

Capture of CO_2 with no/small energy penalty

Negative energy penalty for process[1] (T outlet reduced from e.g. 1200 – 950°C)

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

More efficient heat transfer and more benign conditions

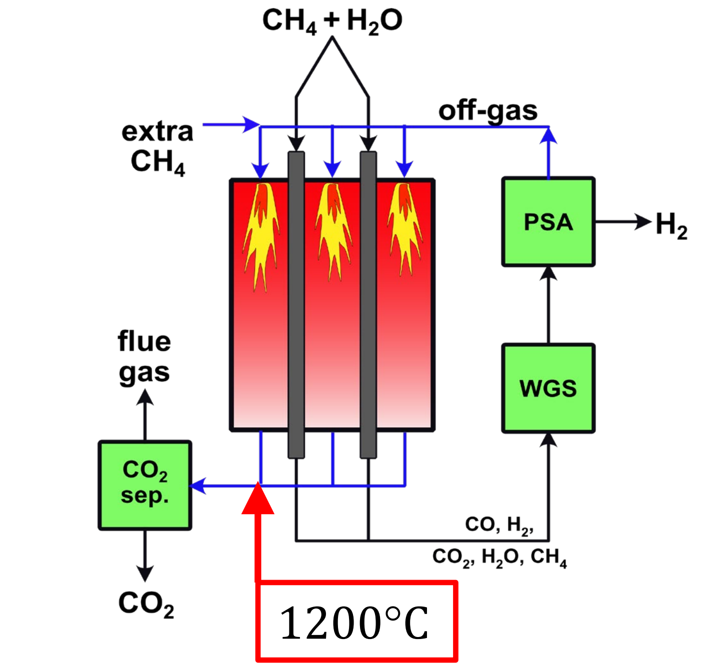
- smaller tube diameter possible in FBHEs (fluidized-bed heat exchangers)
- thus, shorter and thinner tubes (length decrease by factor 3 ?)[2]
- thus, less catalyst (amount decreased by factor of 3 ?)[2]
- thus, lower cost of reforming step

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.

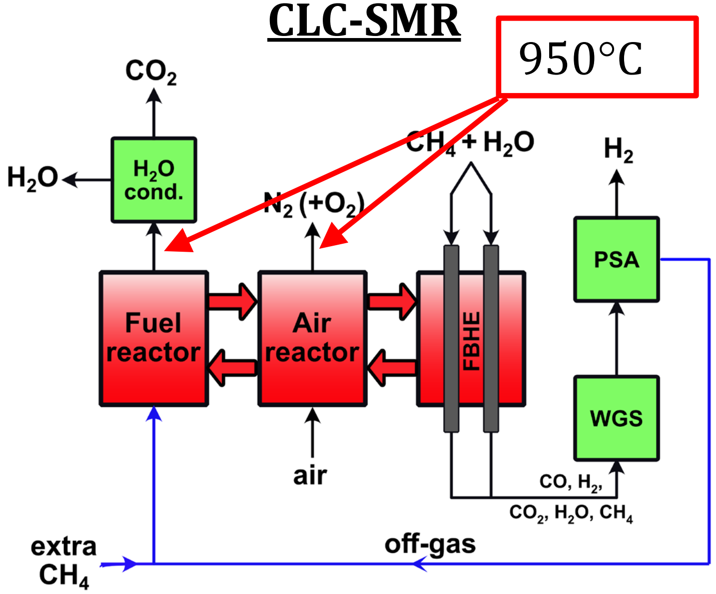
1) Stenberg V, Spallina V, Mattisson T, Rydén M. Techno-economic analysis of H_2 production processes using fluidized bed heat exchangers with steam reforming – Part 2: Chemical-looping combustion. *International Journal of Hydrogen Energy* **46** (2021) 25355-25375

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

<u>Steam Methane Reforming (SMR)</u>



<u>CLC-SMR</u>



Commercial CLC plant
–
Three critical aspects that must have adequate solution

1) **An oxygen carrier that works ☑**

2) **Adequate circulation**

3) **Downstream treatment of gas from fuel reactor to achieve a CO_2 that fulfills purity requirements for transportation/ storage**

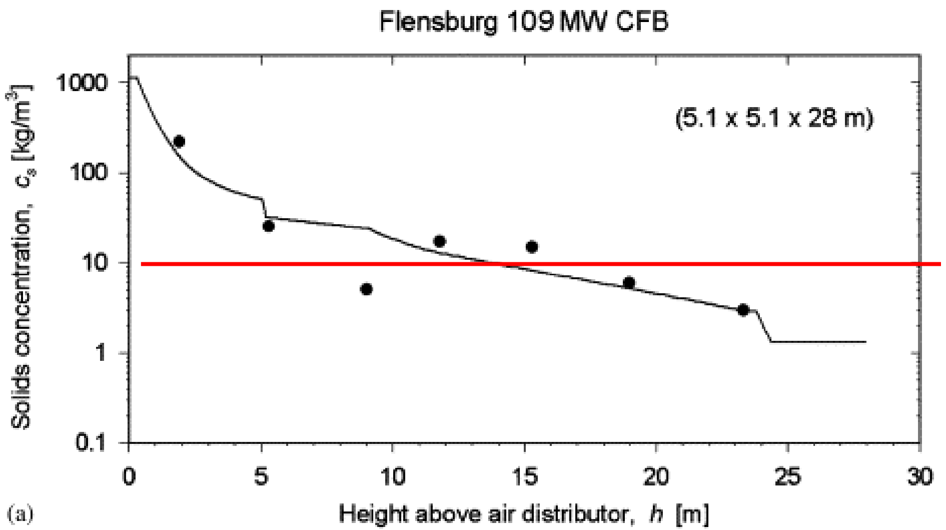
2) What is the circulation in commercial CFBs ?

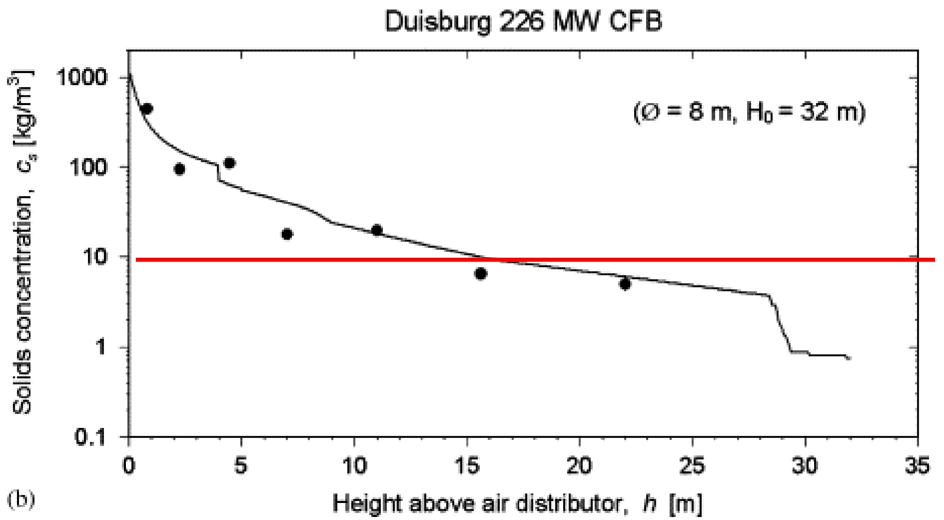
Upwards flow proportial to solids concentration ρ_s (kg/m3)

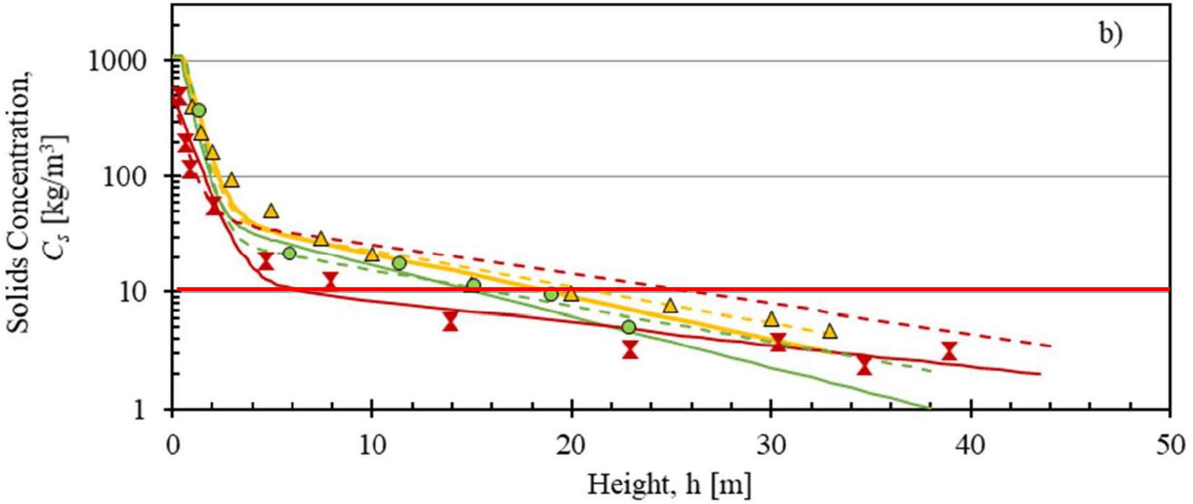
$$G_s = \rho_s(u_0 - u_s)$$

Needed circulation for Chemical-Looping Combustion needs:

$\rho_s \geq 10$ kg/m^3







Solids concentration versus height for 3 CFB boilers. ▲ Emile Huchet, • Zibo, ⧗ Turow.

Solids concentration versus height. Data from two CFB boilers

Conclusions

Actual circulation in CFB boilers is 5-50% of what is needed for CLC

Raised gas velocity not an option due to damage to boiler walls.

With smaller particle size, upwards flow can be dramatically increased.
But will the actual circulation also increase ? Increased loss in cyclone?

As noted, upwards flow decreases exponentially with height.

However, ***collection of down-flow along the walls, would be sufficient***.

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

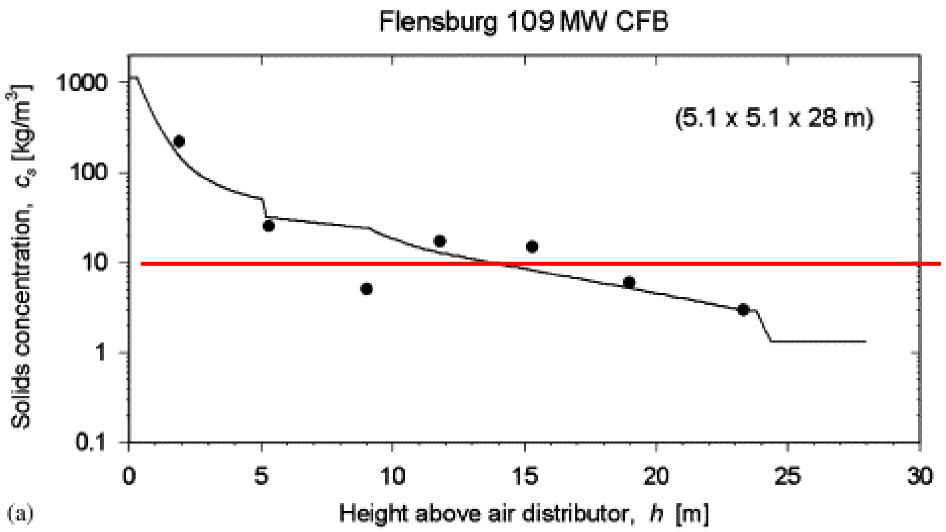
2) But upwards flow in lower part is sufficient

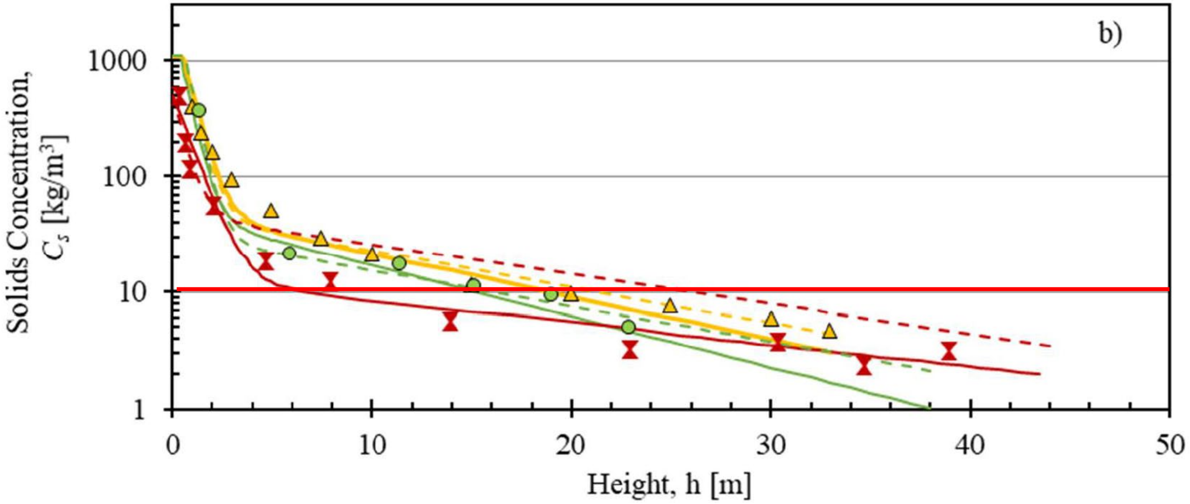
Upwards flow proportial to solids concentration (kg/m3)

$$G_s = \rho_s(u_0 - u_s)$$

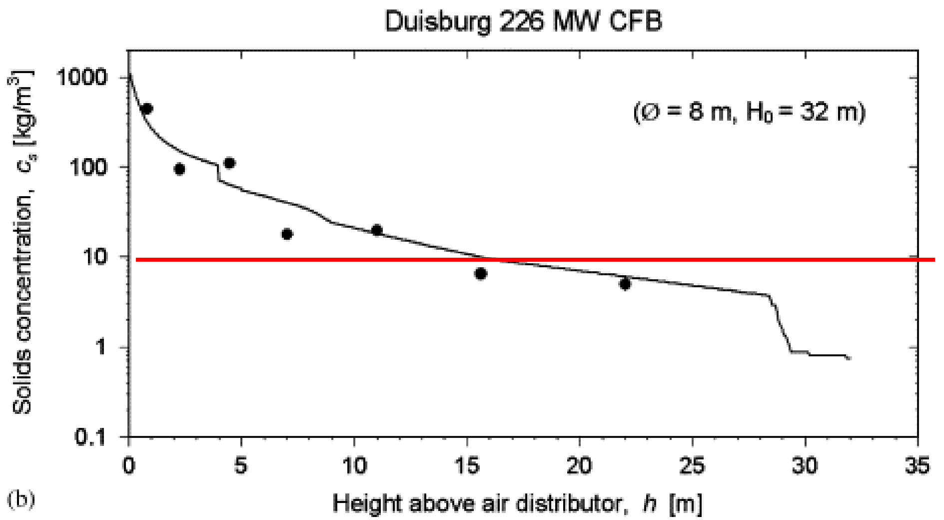
Needed circulation for Chemical-Looping Combustion needs:

$\rho_s \geq 10\ kg/m^3$



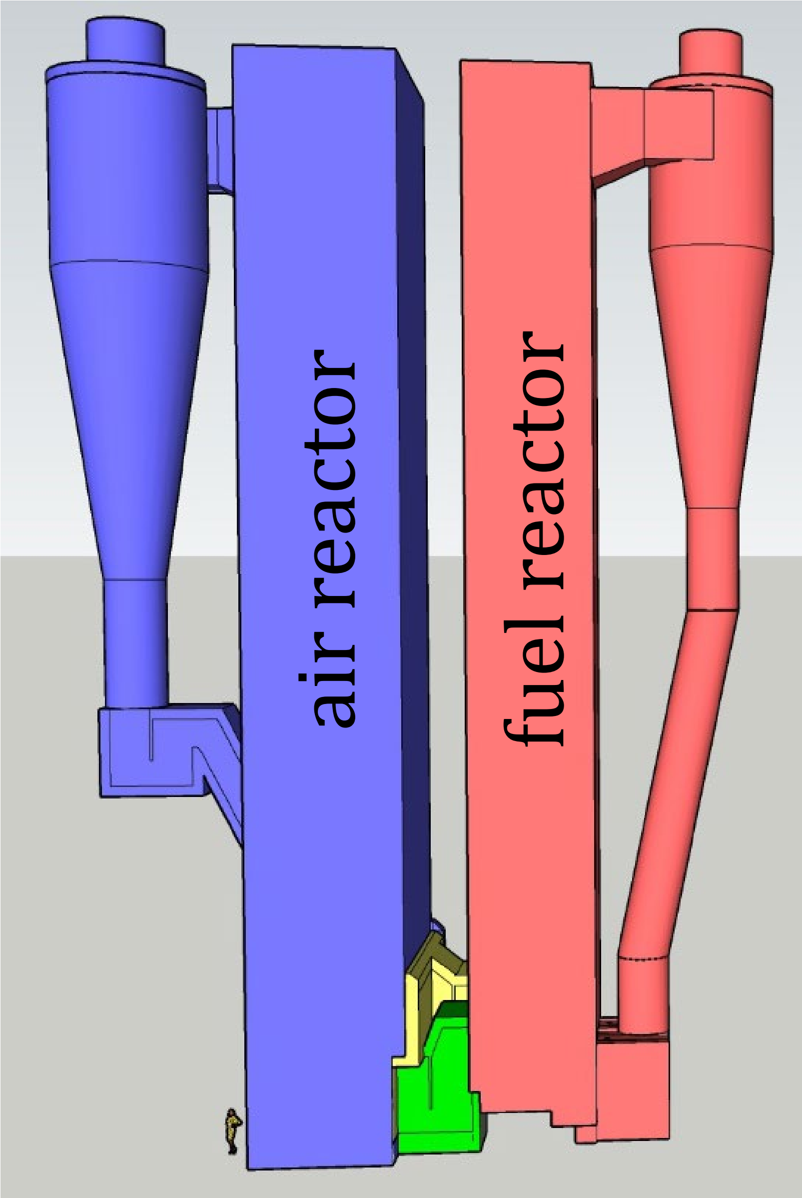


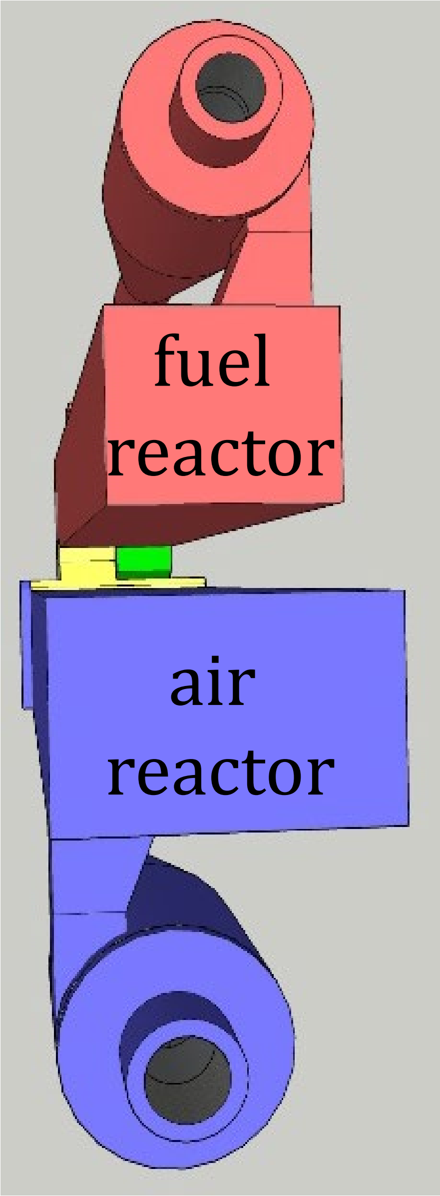
Solids concentration versus height for 3 CFB boilers. ▲ Emile Huchet, ● Zibo, ⧗ Turow.



Solids concentration versus height. Data from two CFB boilers

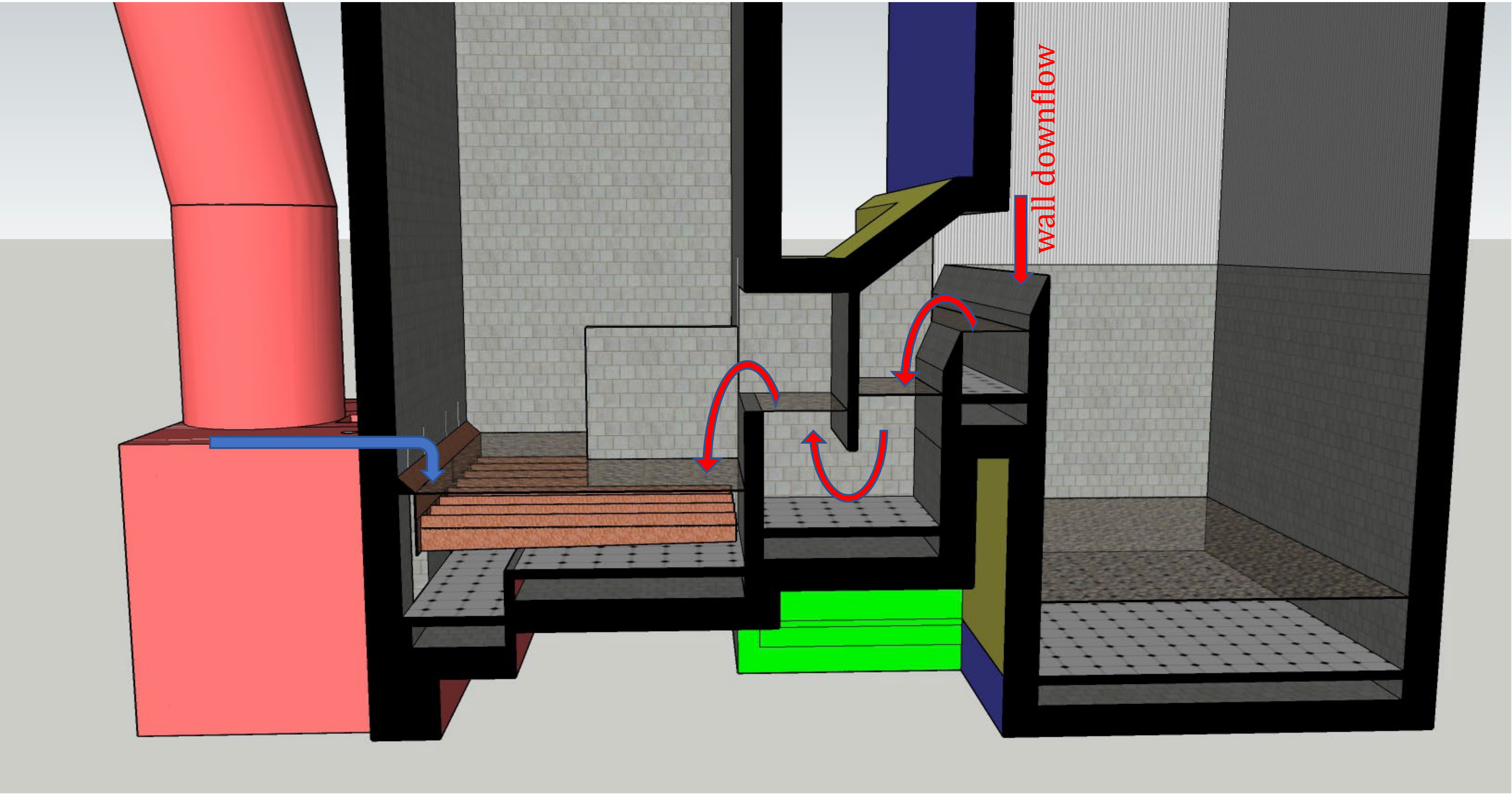
200 MW CLC-CFB boiler, 40 m high





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

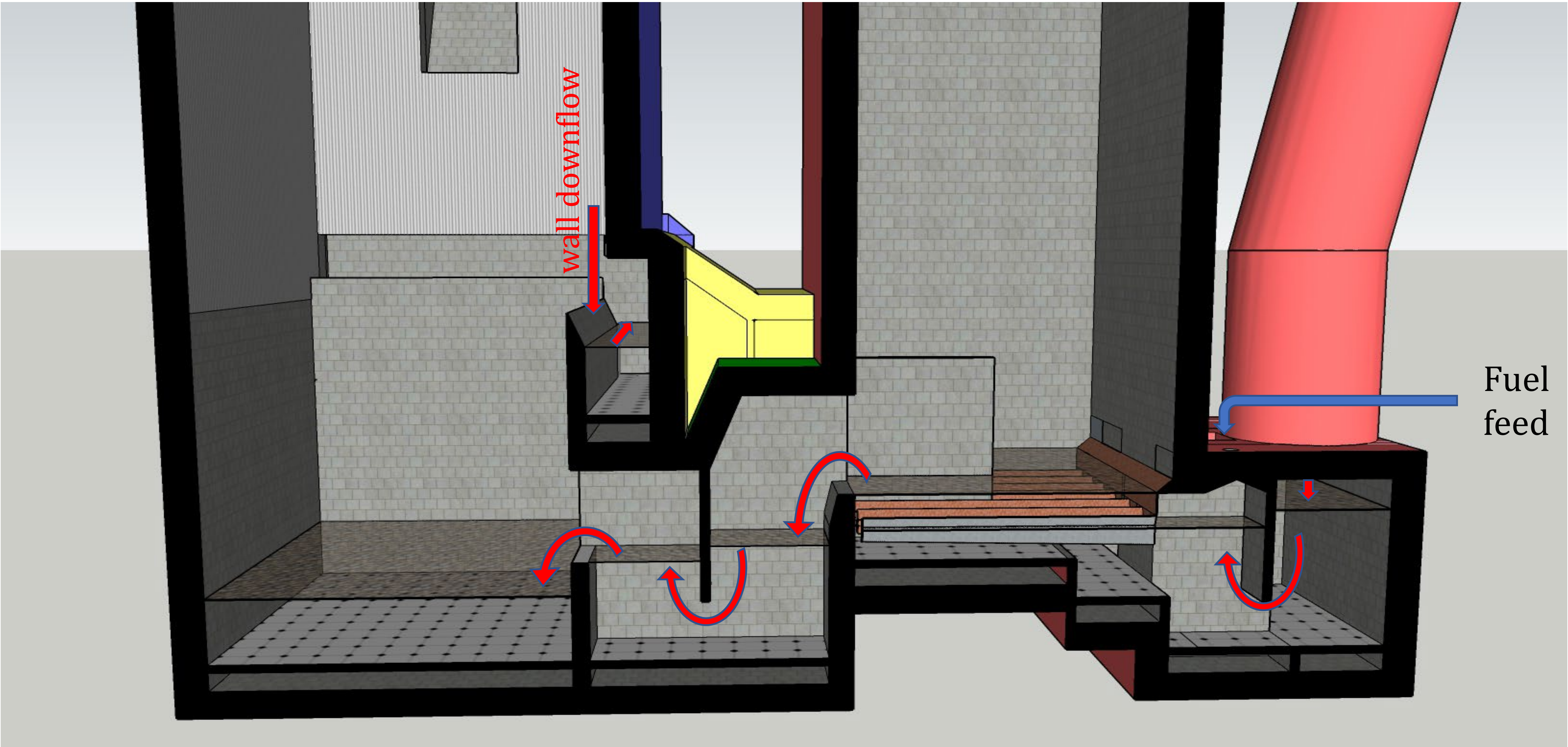
Loopseal leading from air reactor to fuel reactor



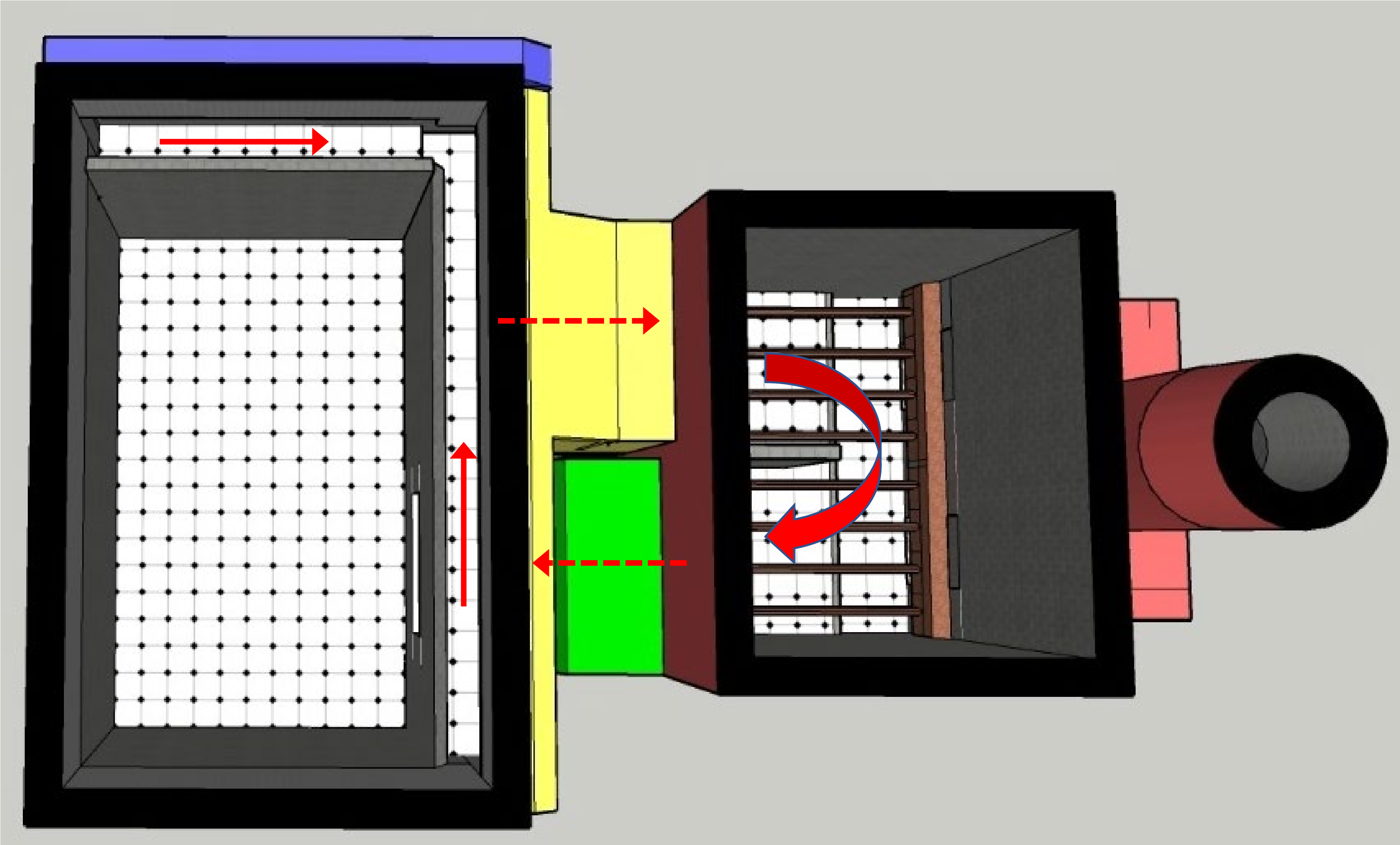
fuel reactor

air reactor

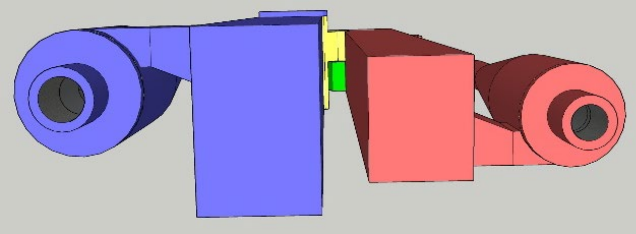
Loopseal leading back from fuel reactor to airfuel reactor



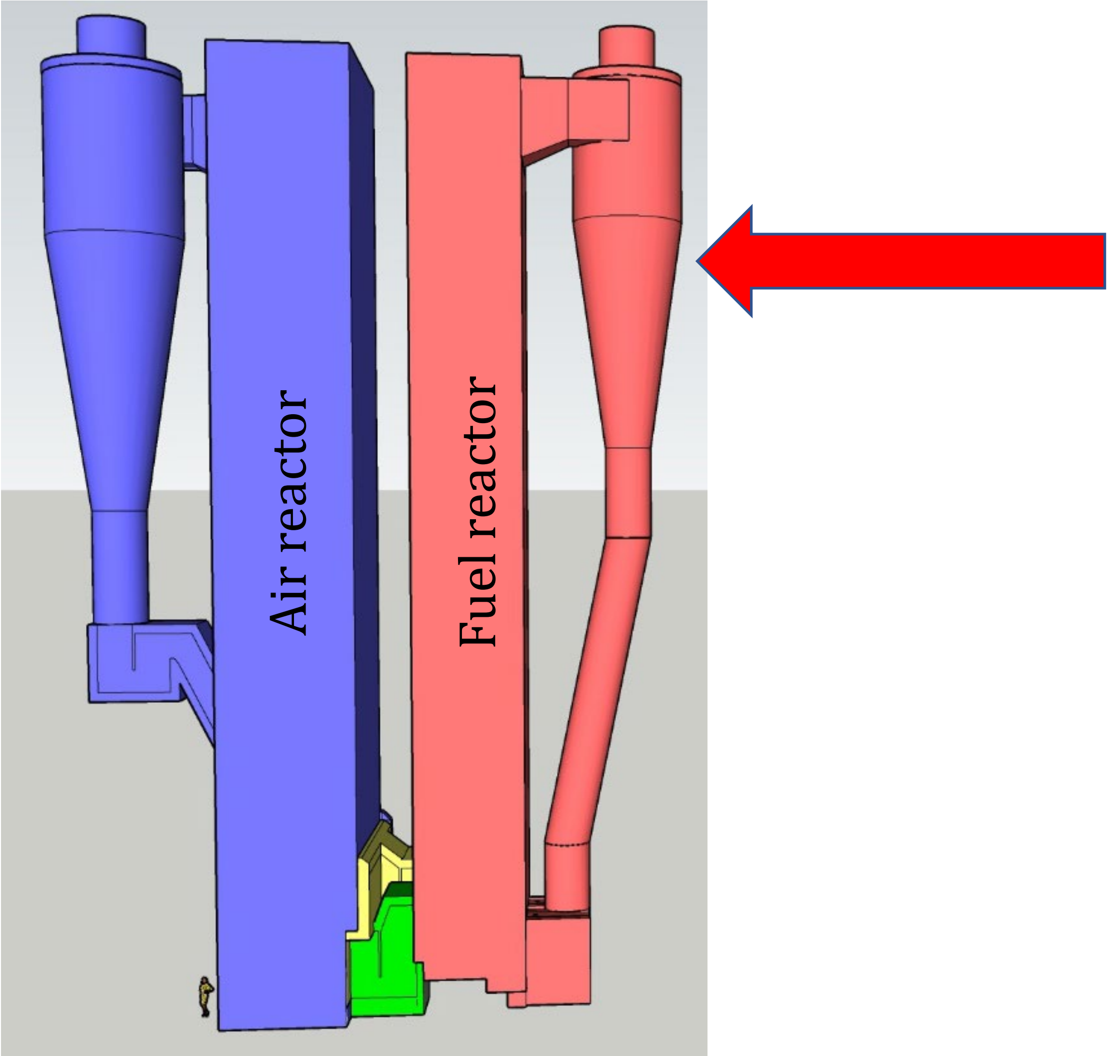
air reactor fuel reactor

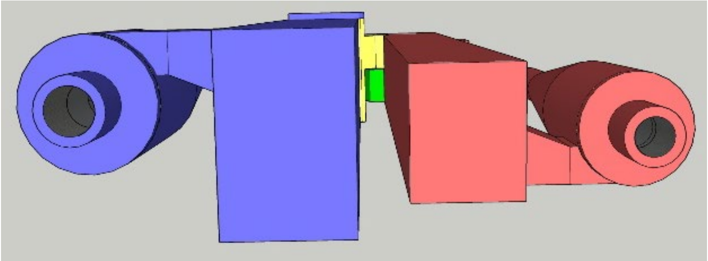


air reactor



fuel reactor





200 MW CLC-CFB, added cost of Fuel Reactor:
1500 m² insulated wall
at
2000 €/m²

>>> 3 M€

or

0.3 M€/year

capture: 0.4 Mt CO_2/year

cost of fuel reactor : **0.75 €/t CO_2**

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

3) Purification of CO2 stream

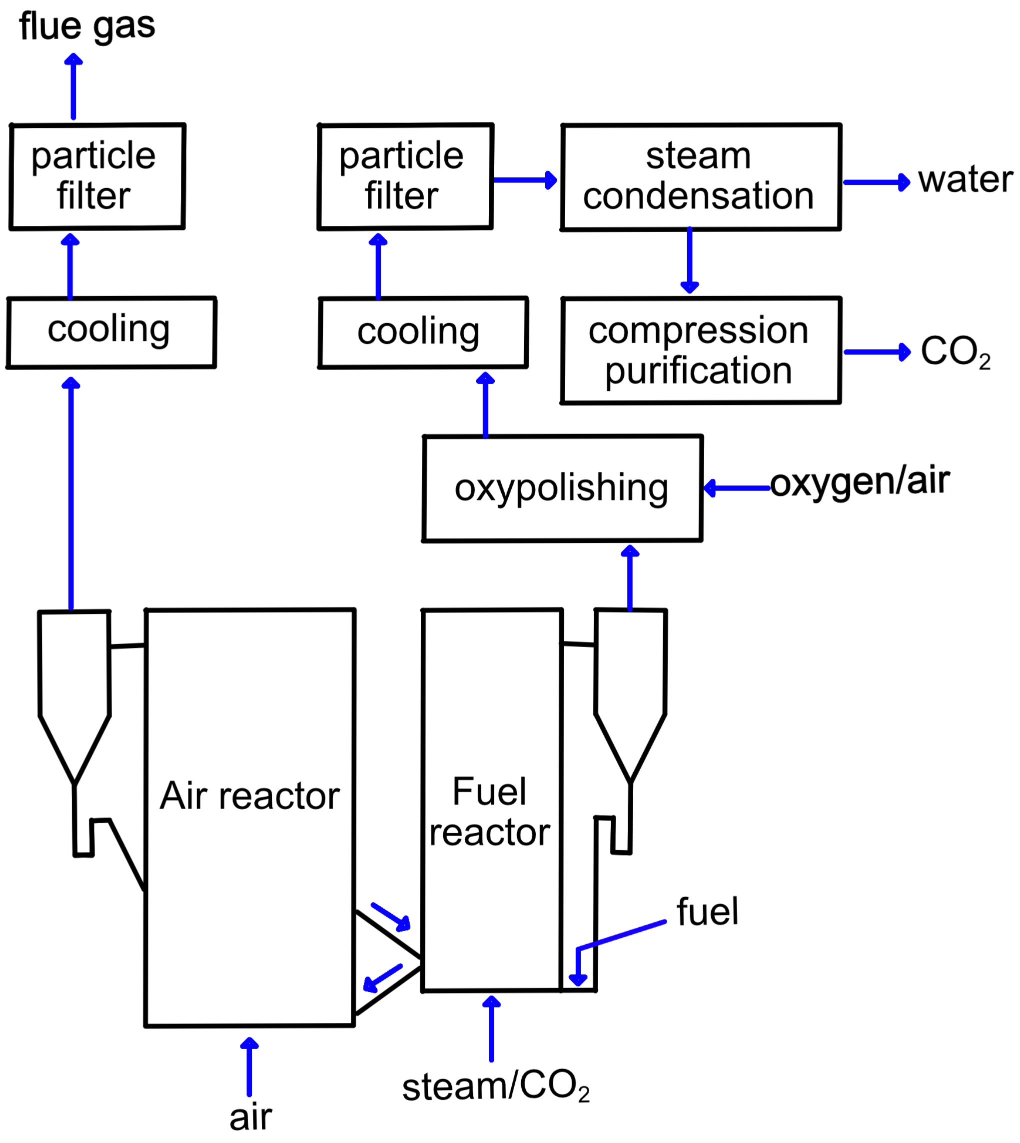


Table 2. Required purity of CO_2. [69, 70]

Component	ppm
Water, H_2O	≤30
Oxygen, O_2	≤10
Sulphur oxides, SO_x	≤10
Nitric oxide/nitrogen dioxide, NO_x	≤10
Hydrogen sulphide, H_2S	≤9
Carbon monoxide, CO	≤100
Amine	≤10
Ammonia, NH_3	≤10
Hydrogen, H_2	≤50
Formaldehyde	≤20
Acetaldehyde	≤20
Mercury	≤0.03
Cadmium + Thalium (sum)	≤0.03

Measures for purification

1) Elimination of in-leakage

Downstream costs for removal of air ingress are very high.

Should not be a major technical issue to assure no, or very low, air ingress.

- Construction measures to assure no inleakage
    - Moving joints can use bellow seals and barrier gas (CO_2)
    - Measures to seal discharge of fly-ashes
- Strict protocols for avoiding mistakes leading to air ingress
- Careful monitoring of gas purity, to detect and address any inleakage

2) Removal of SO_2

Any SO_2 present must be removed by wet flue gas desulphurization. Can be done in connection with water removal. Concentrated stream lowers costs, whereas need for high purity increases costs.

3) Removal of NO_x

Likely not needed:

- Partly reduced oxygen carrier ilmenite is efficient in reducing NO.
- Only way of NO formation is by oxidation fuel nitrogen by oxygen carrier.
- Equilibrium NO concentration in fuel reactor below 0.001 ppm

If needed:

- Conventional Selective Catalytic NOx Reduction.
    - High reduction not possible
    - Incoming NO needs to be low
- Co-removal of NO and SO_2, at pressure, e.g. 30 bar.
    - Oxygen must be present
    - Deep reduction not possible, incoming NO must be low
    - Not commercial technology
- Addition of Cl_2O, to the co-removal system
    - Deeper reduction possible
    - Not commercial technology
- Distillation of CO_2

4) Removal of O_2

Catalytic combustion

- at high temperature with CH_4
- at lower temperature with H_2

5a) Compression with single flash separation

With flash separation compounds of low solubility, e.g. N_2, NO, O_2, can be partly removed, depending on pressure.
Could be sufficient, if concentrations of gases that need deep reduction is low enough.
Power need 2.9 - 3.8% of fuel heating value (coal),

5b) Compression with cryogenic distillation

Remove gases with low solubility in CO_2 to ppm levels.
Removal steps 3) NO and 4) O_2 not needed.
Power need 7% of fuel heating value (coal)
Necessary if NO cannot be lowered enough in 3)

6) Drying of CO_2
Water can be removed using molecular sieves or a dessicant, e.g. triethylene glycol

Commercial CLC plant
–
Three critical aspects that must have adequate solution

1) **An oxygen carrier that works ☑**

2) **Adequate circulation ☑**

3) **Downstream treatment of gas from fuel reactor to achieve a CO_2 that fulfills purity requirements for transportation/ storage ☑**

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 and 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

Thank you!