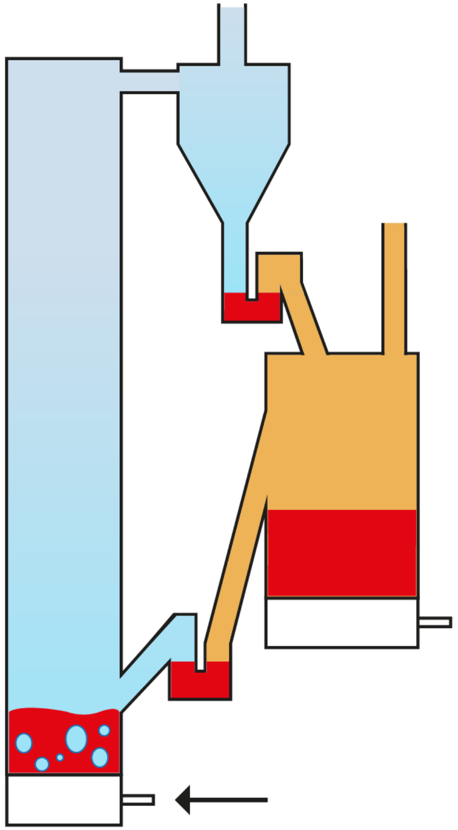
Chemical-Looping Combustion
-
Applications and Three Important Aspects:
Oxygen Carrier,
Circulation
and CO_2 Downstream Treatment.



Anders Lyngfelt

6th International Conference on Chemical Looping
September 19-22, 2022
Zaragoza, Spain

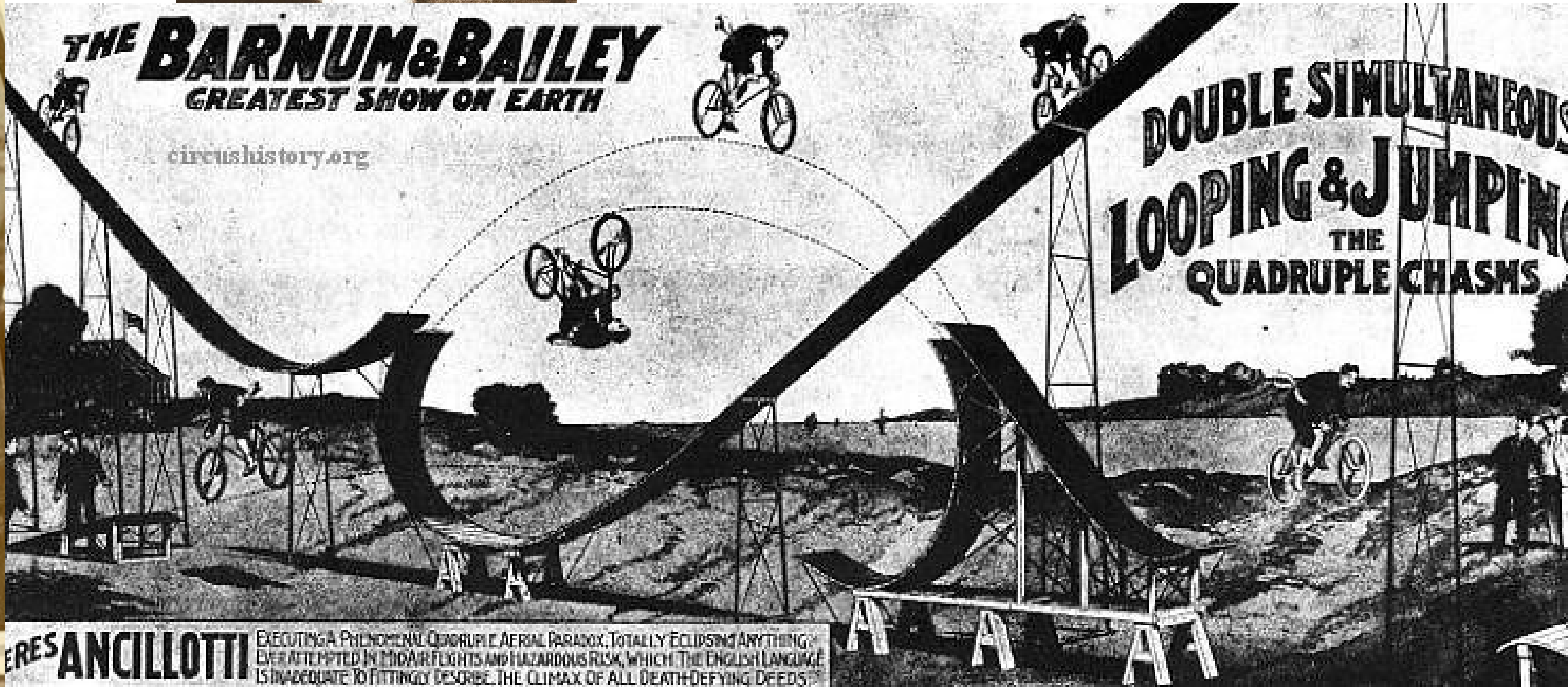
CHALMERS

History of looping cycles

1st demonstrations by:

Diavolo 1902

and Ugo Ancillotti 1904 (double loop)



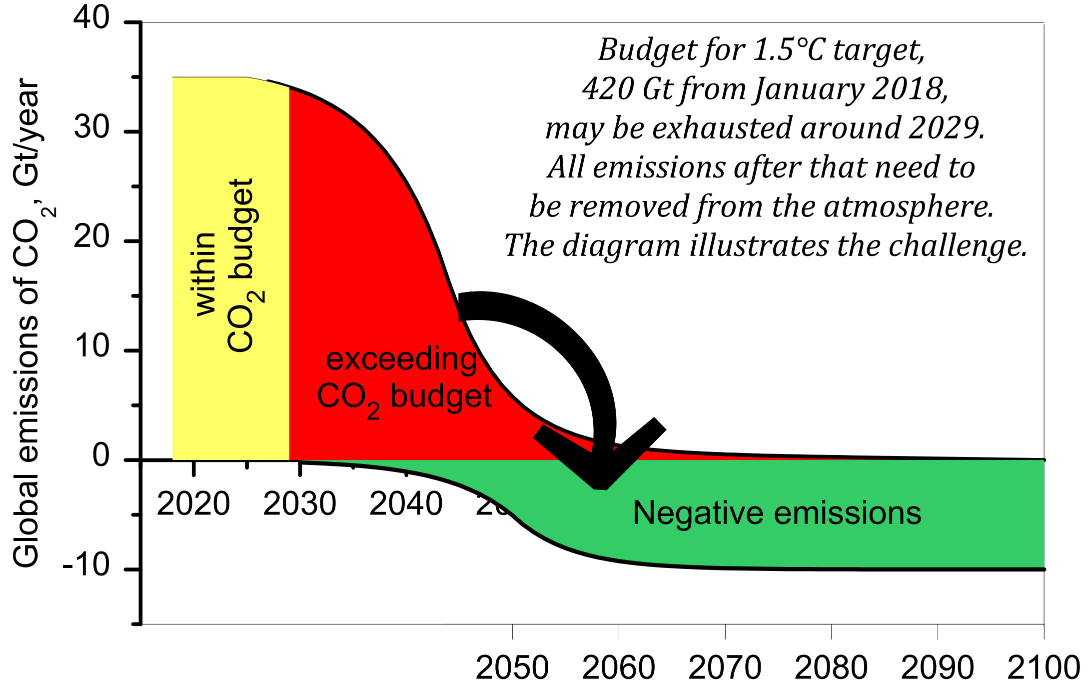
Most important applications of CLC technology

- Coal combustion
  - similarity to normal circulating fluidized bed technology
  - small added cost, low energy penalty
  - concentration of pollutants 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

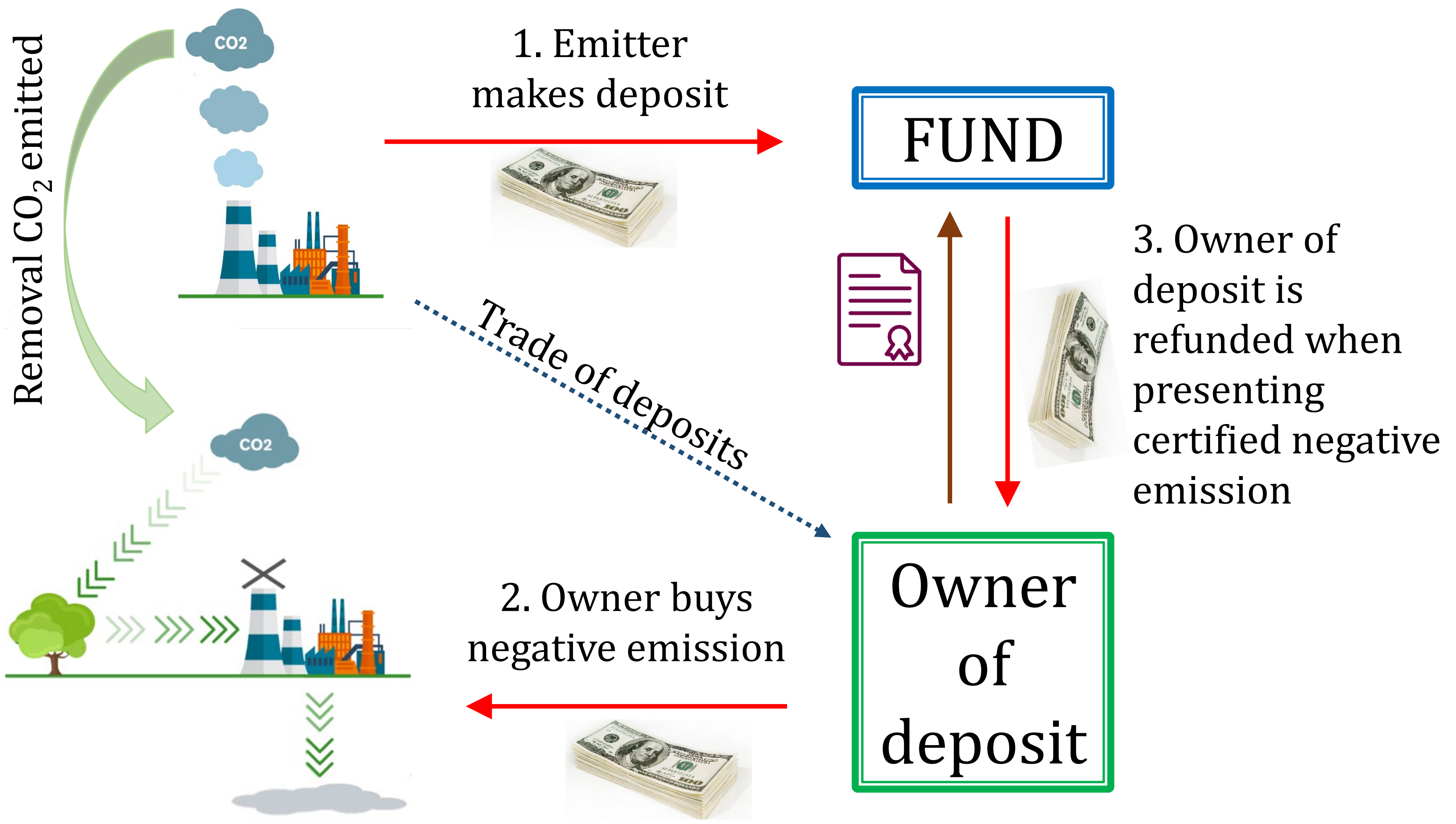
- Biomass combustion
  - same advantages as in coal combustion above
  - in addition potential advantage wrt alkalis
  - to meet climate targets gigantic negative emissions are needed

- Steam-Methane Reforming with Chemical-Looping Combustion (SMR-CLC)
  - potential for negative cost and energy penalty
  - vast future market for decarbonizing natural gas

- 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.

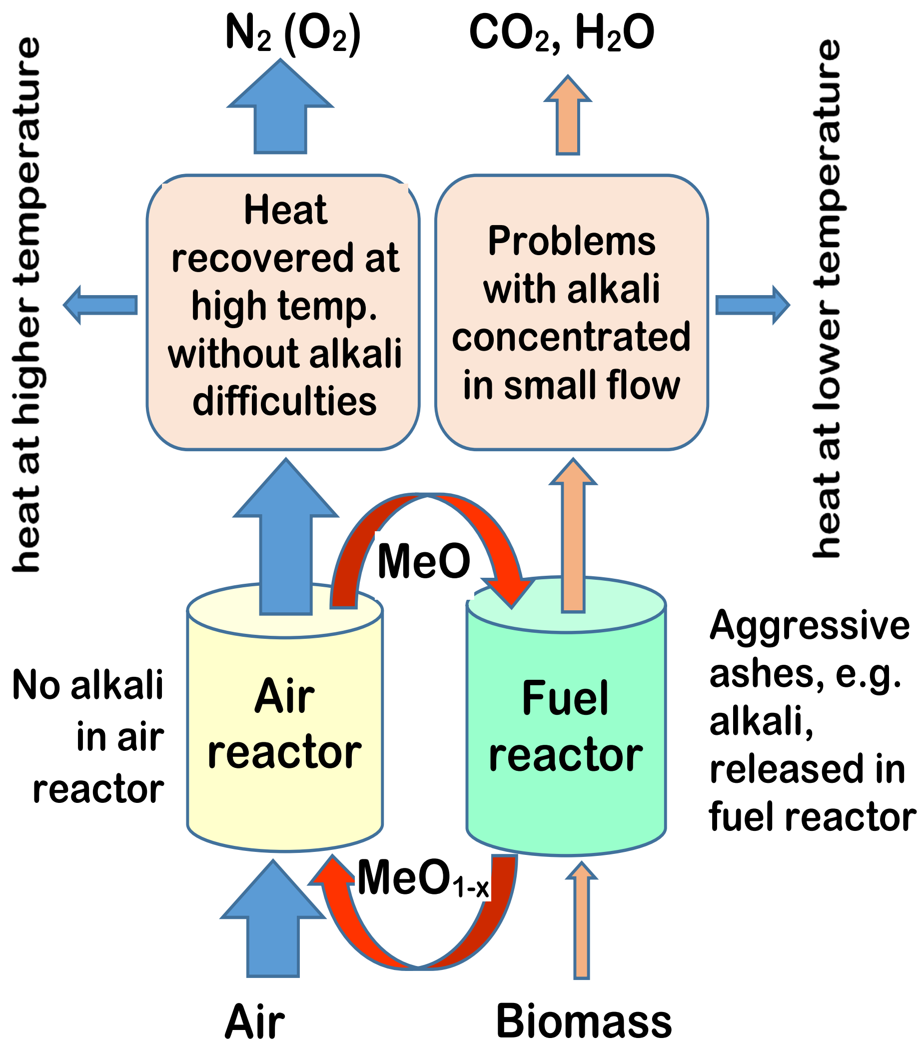


Atmospheric CO_2 Removal Deposits (ACORDs)



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 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 75 MW CFB with ilmenite

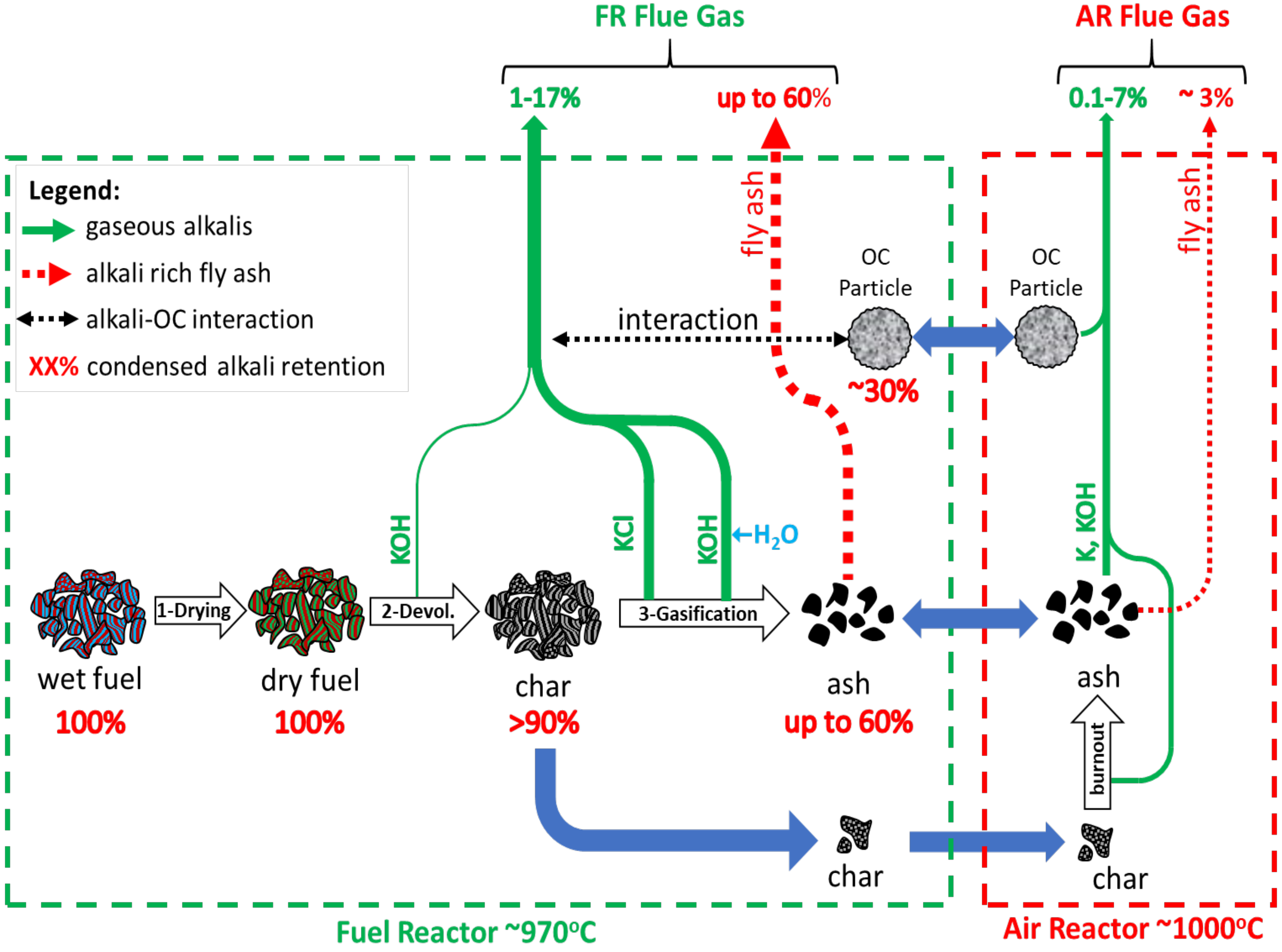
Could range of possible fuels be extended to more difficult fuels?

Similarly, NO in concentrated flow. Options for eliminated/reduced NO ?

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 should be mostly free of KCl

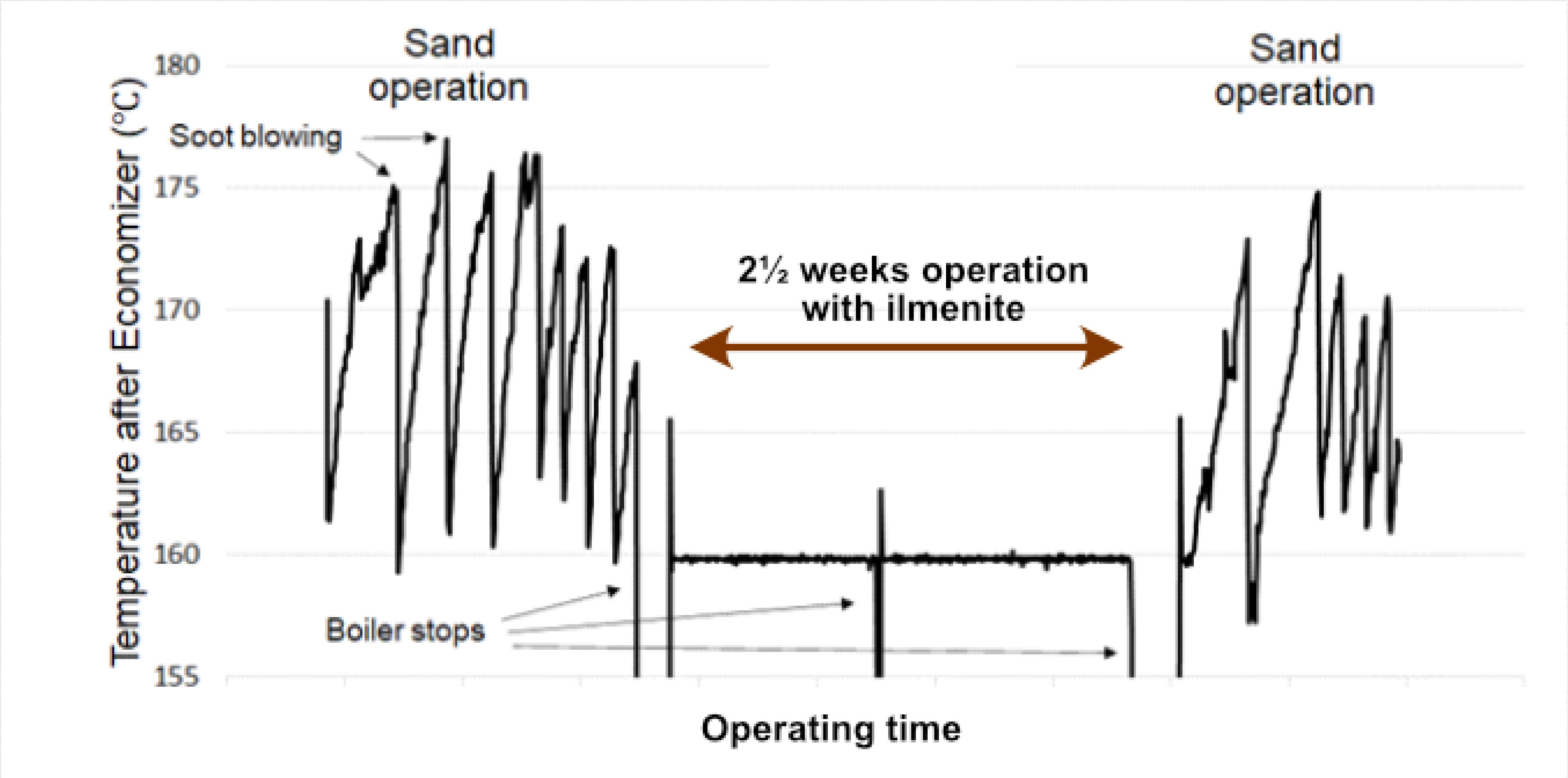
More in session 1A: Ivan Gogolev



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

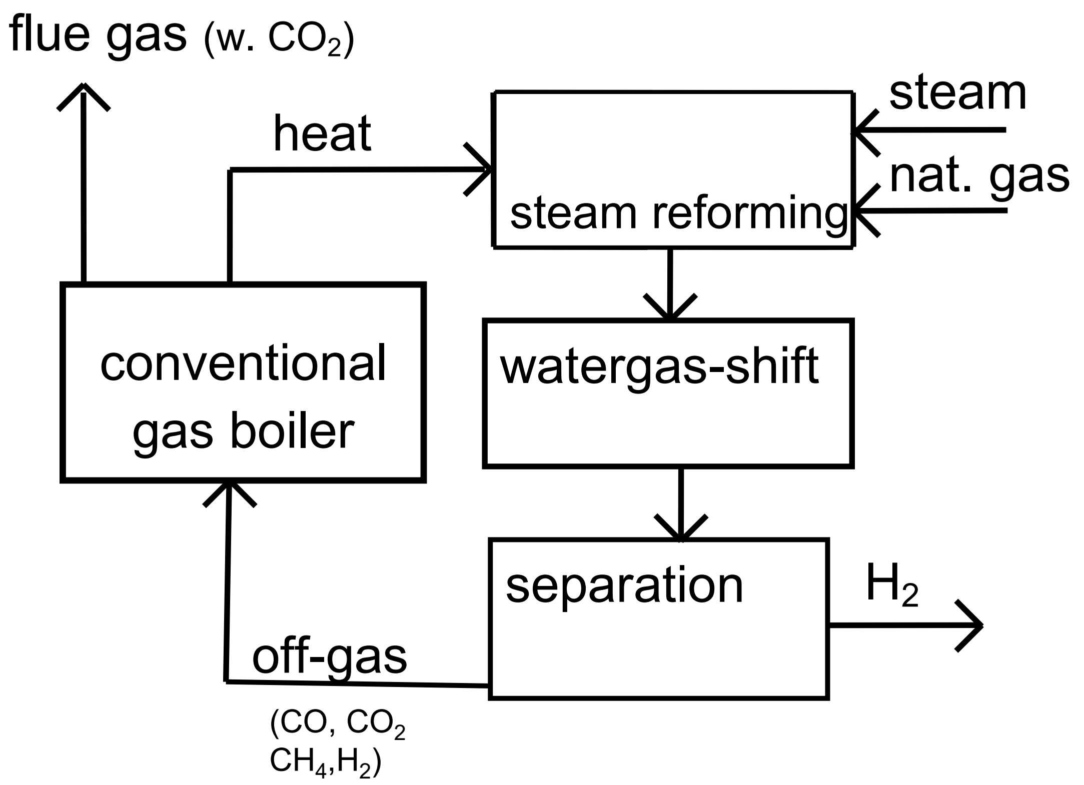
Ivan Gogolev, *The Release, Distribution, and Implications of Alkalis in Chemical Looping Combustion of Biomass*, PhD Thesis, Chalmers University of Technology, Göteborg, Sweden 2022

OCAC (Oxygen Carrier Aided Combustion) operation Chalmers 12 MW CFB

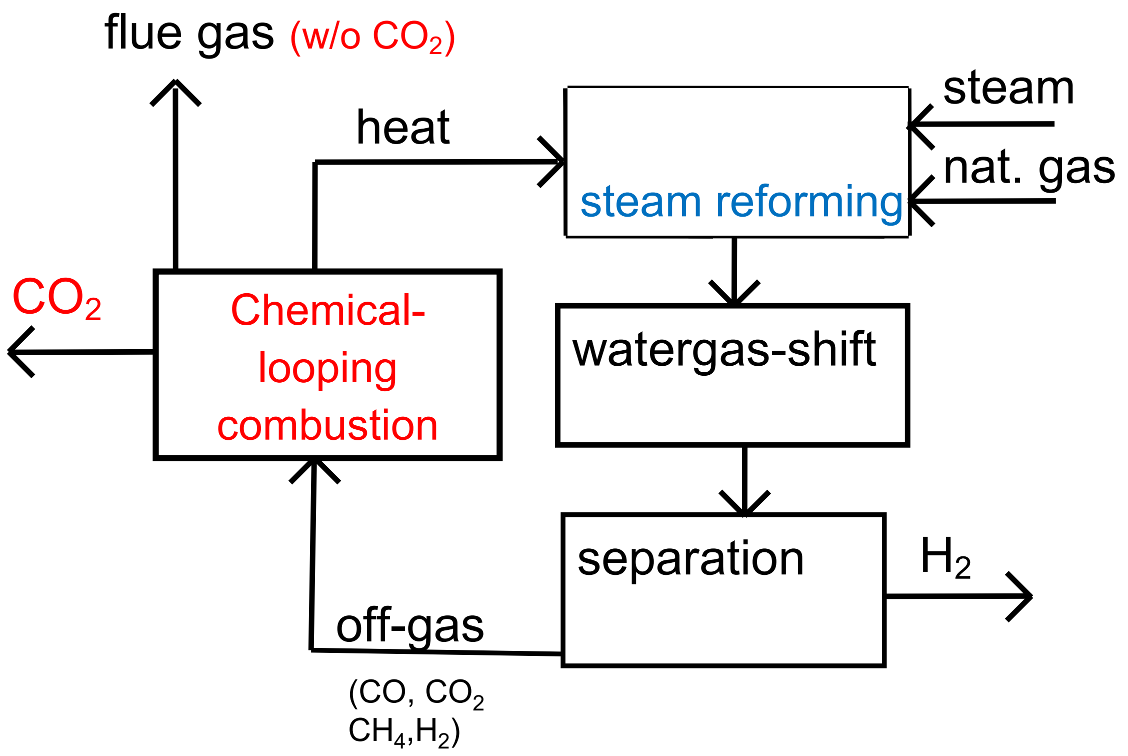


Decarbonizing fossil gas with CLC-SMR

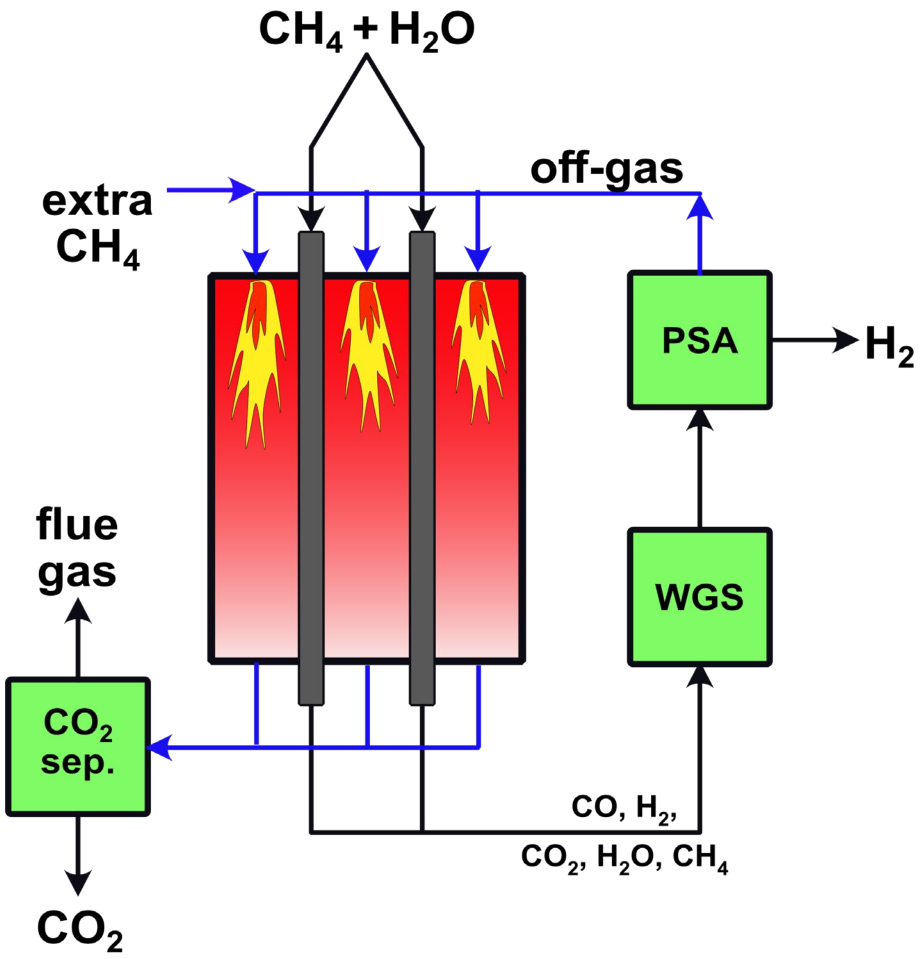
Steam methane reforming (SMR)



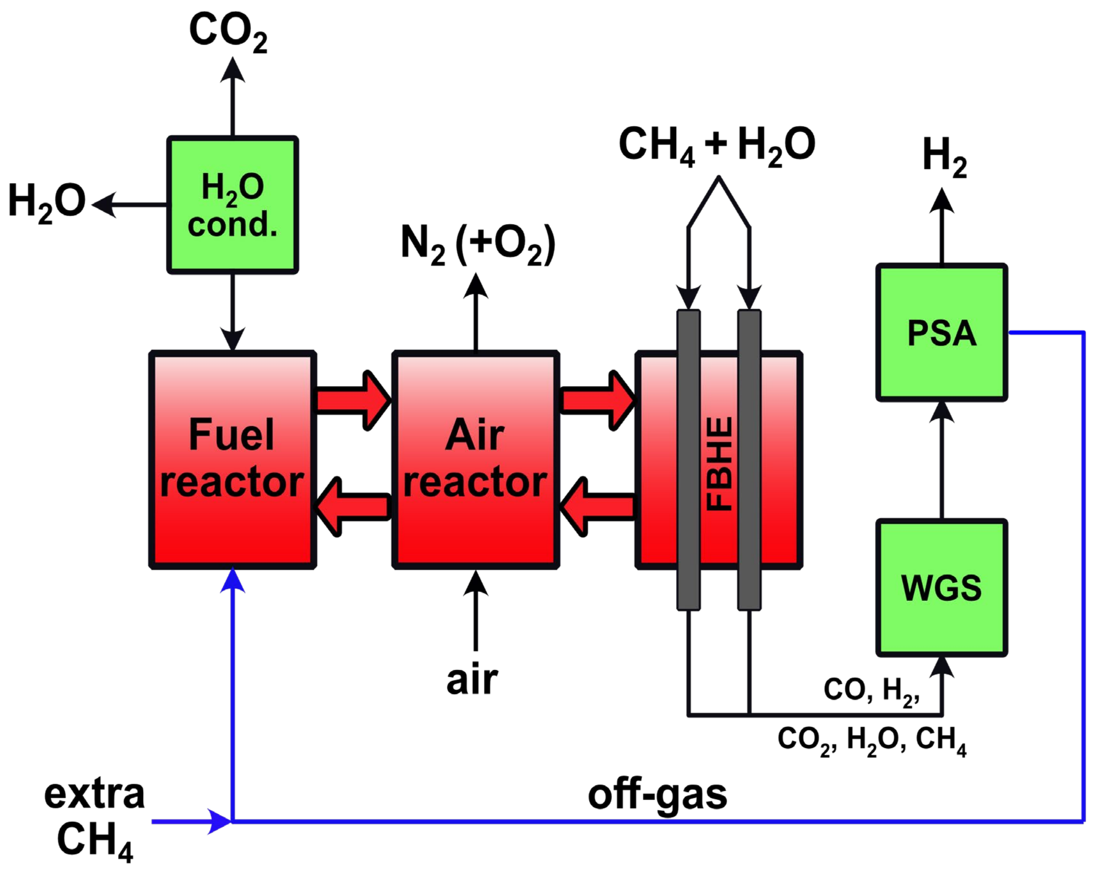
Steam reforming with CLC



Steam Methane Reforming (SMR)



Steam reforming with CLC



Why CLC-SMR?

No/small energy penalty for gas separation

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

No/small equipment and 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
- thus, less catalyst
- thus lower cost of reforming step

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

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

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

How CLC-SMR?

Develop CLC- SMR to commercial scale using three parallel paths

1) Build combined CLC-CFB for biomass, that can also be used for gas

2) Investigate SMR in heated fluidized-bed heat exchangers

3) High gas conversion desired in CLC-SMR (we do not want heat in the outlet gases), two options:

3a) Develop large scale manufacture of $CaMnO_3$ (temperature a bit to high for CuO-materials)

3b) Pass the gas (off-gas + additional CH_4) through a reformer to convert CH_4 to CO and H_2

- gives positive reaction enthalpy in fuel reactor
- low-cost oxygen carrier can be used (manganese ore and/or ilmenite)

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**

1) Oxygen carriers

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

- a significant number of materials that work
- includes 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, shows it can be used at industrial conditions

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

Lyngfelt, A., Brink, A., Langørgen, Ø., Mattisson, T., Rydén, M., and Linderholm, C., 11,000 h of Chemical-Looping Combustion Operation – Where Are We and Where Do We Want to Go?

Andersson, B.-Å., Lind, F., Corcoran, A., Thunman, H., 4000 Hours of Operation with Oxygen-Carriers in Industrial Relevant Scale (75 MWth), *4th International Conference on Chemical Looping, September 26-28, 2016, Nanjing, China*

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

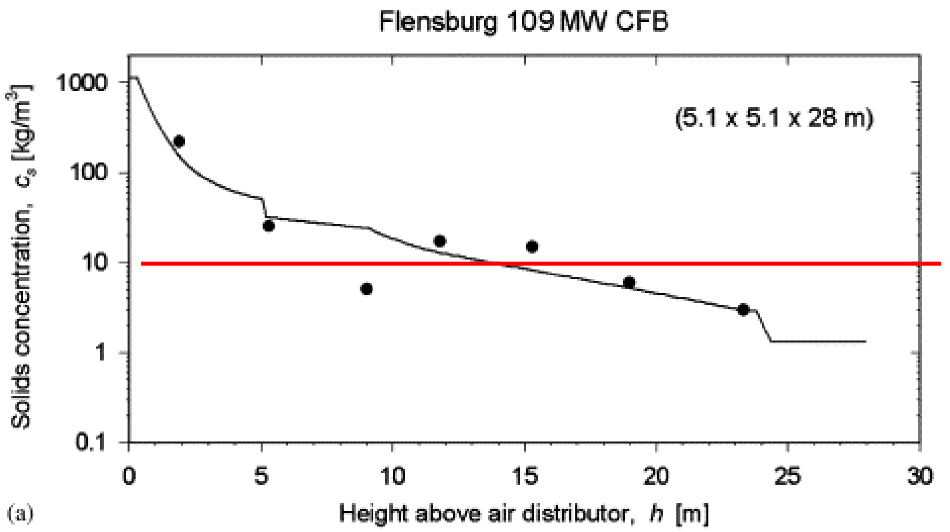
2) What is the circulation in commercial CFBs ?

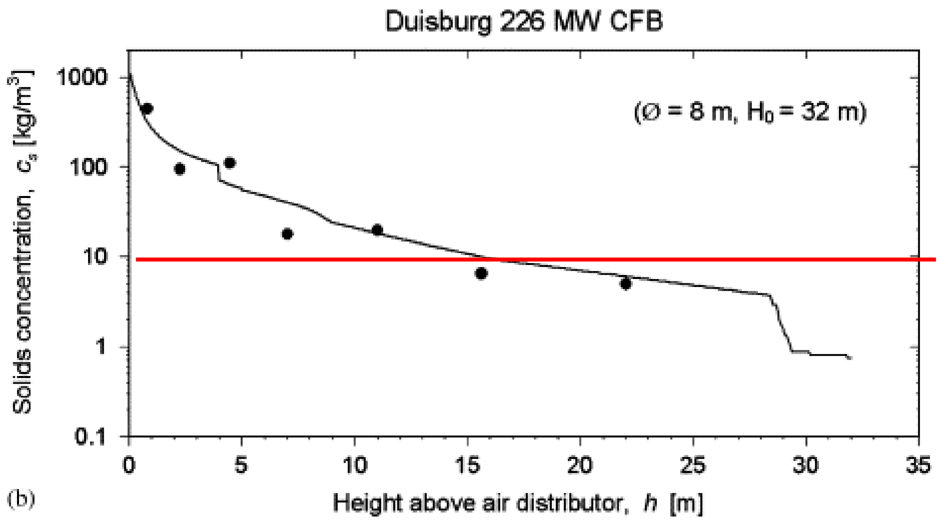
Upwards flux in kg/m²s: $G_s = \rho_s(u_0 - u_s)$

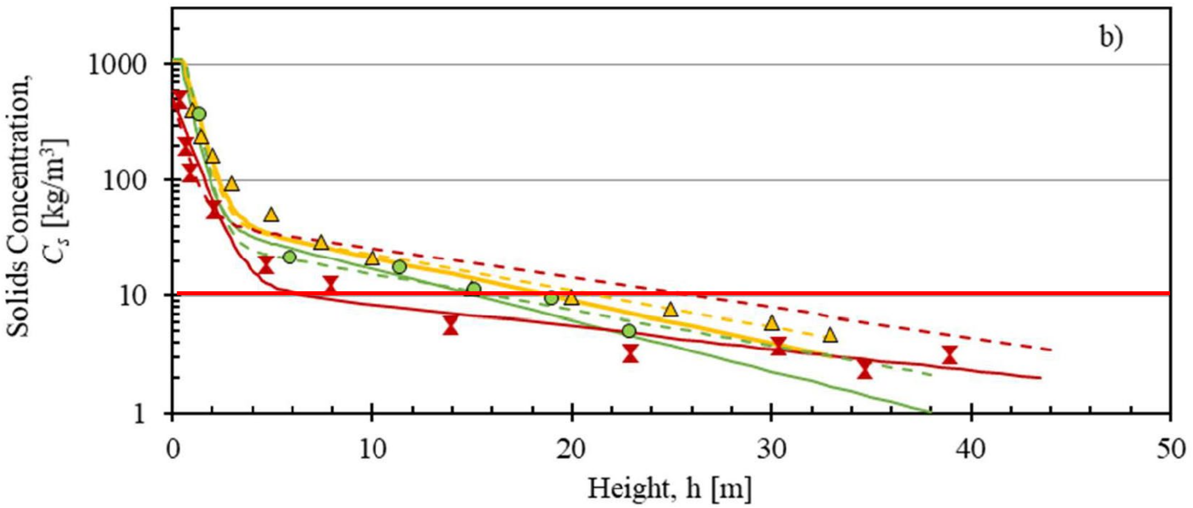
Needed circulation for Chemical-Looping Combustion:
40 kg/m²s

If $(u_0 - u_s)$ = 4 m/s

$\rho_s \geq 10$ kg/m³





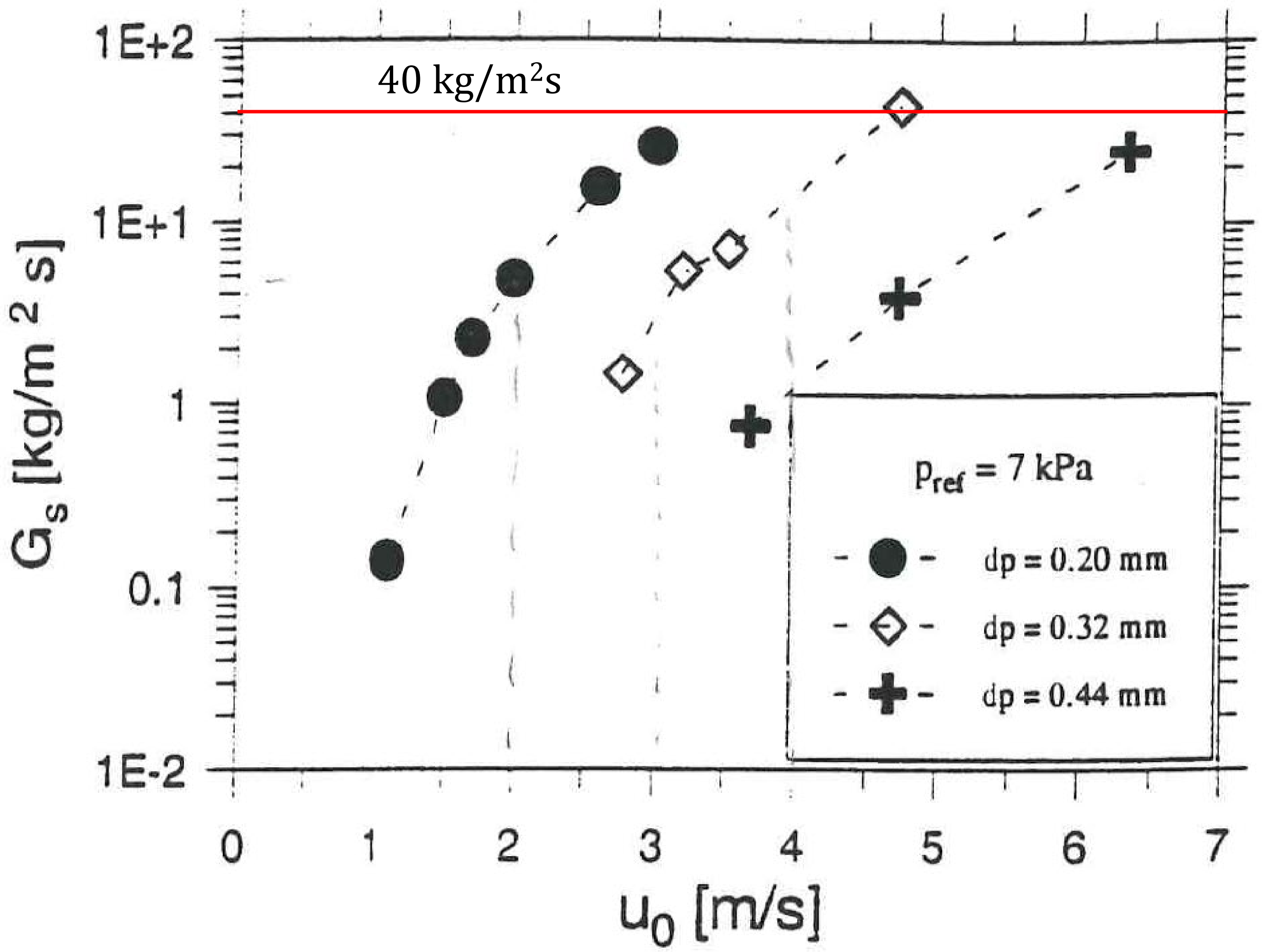


Solids concentration versus height for 3 CFB boilers. ▲ Emile Huchet, • Zibo, ⧗ Turow.

Solids concentration versus height. Data from two CFB boilers

Solids flux in top of 12 MW CFB (Chalmers)

(Johnsson 1995)

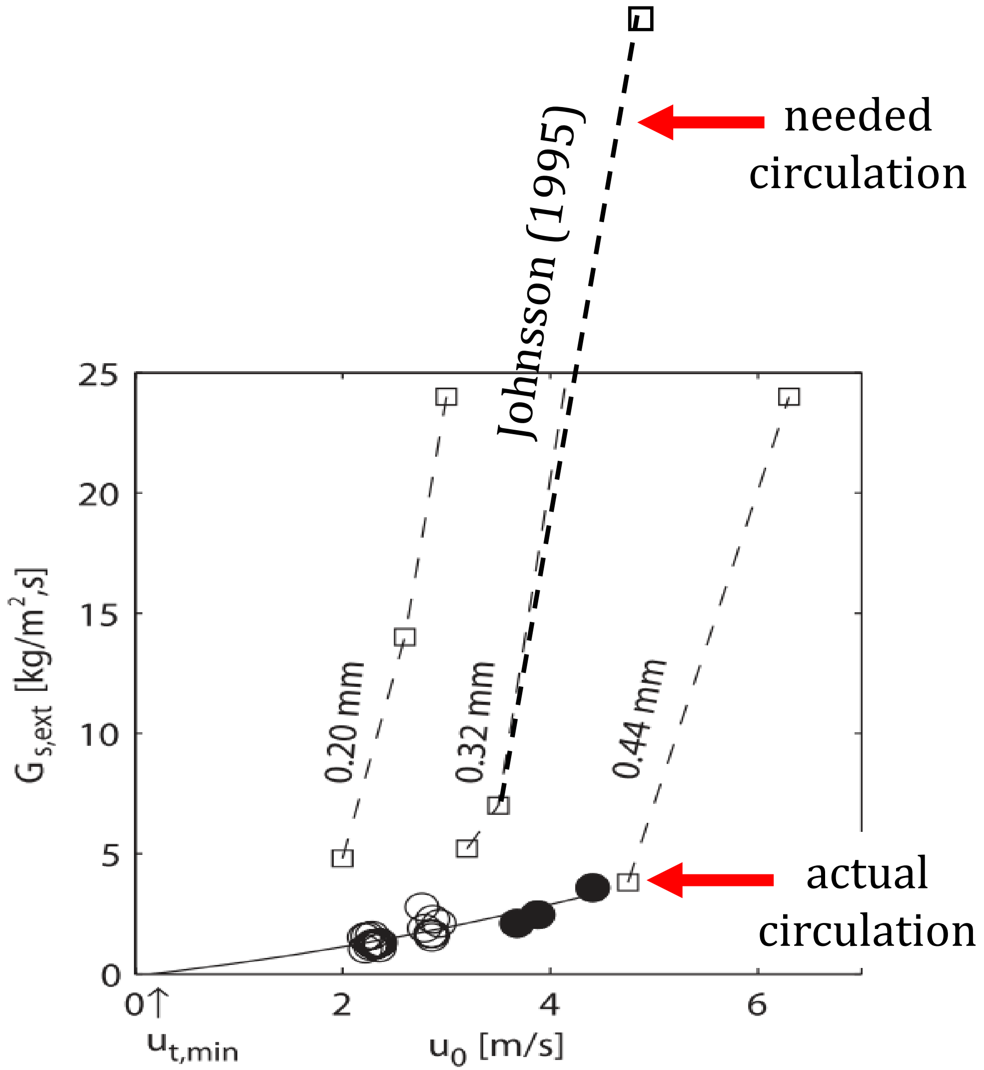


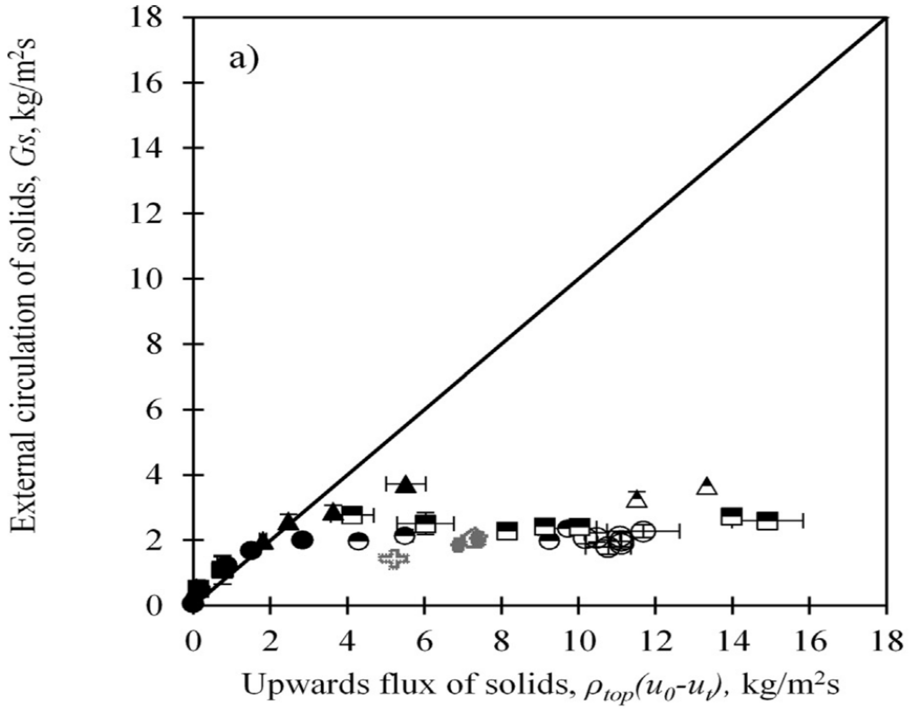
Actual circulation is difficult to measure.

The upwards flow in the top of the riser is often assumed to be the actual circulation.

BUT, the upwards flow in the top,
is not necessarily equal to the flow going into the cyclone

What do we know?





Measured external circulation versus upwards solids flux in the top of a cold-flow model of a 200 MW_{th} CFB. (Djerf 2021)

External (actual) circulation as measured by heat balance (filled + open **circles**), (Edvardsson 2006) Boxes and dashed lines show the **upwards flow** from previous slide. (Johnsson 1995)

Actual circulation:

$$G_s^* = G_{s,top}(1-k_b)$$

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.

Thus, 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

Upwards flow is sufficient below around 10 m height

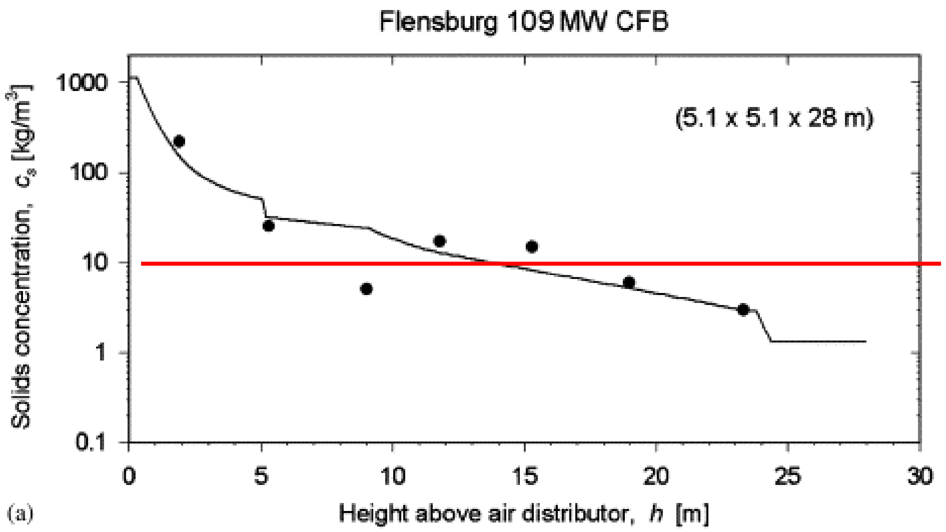
Upwards flux in kg/m^2s: $G_s = \rho_s(u_0 - u_s)$

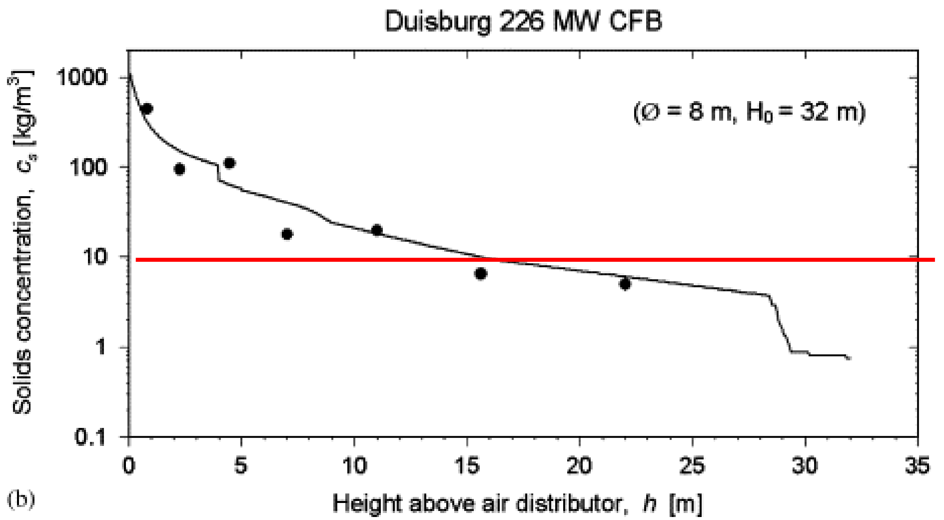
Needed circulation for Chemical-Looping Combustion:

$40\ kg/m^2s$

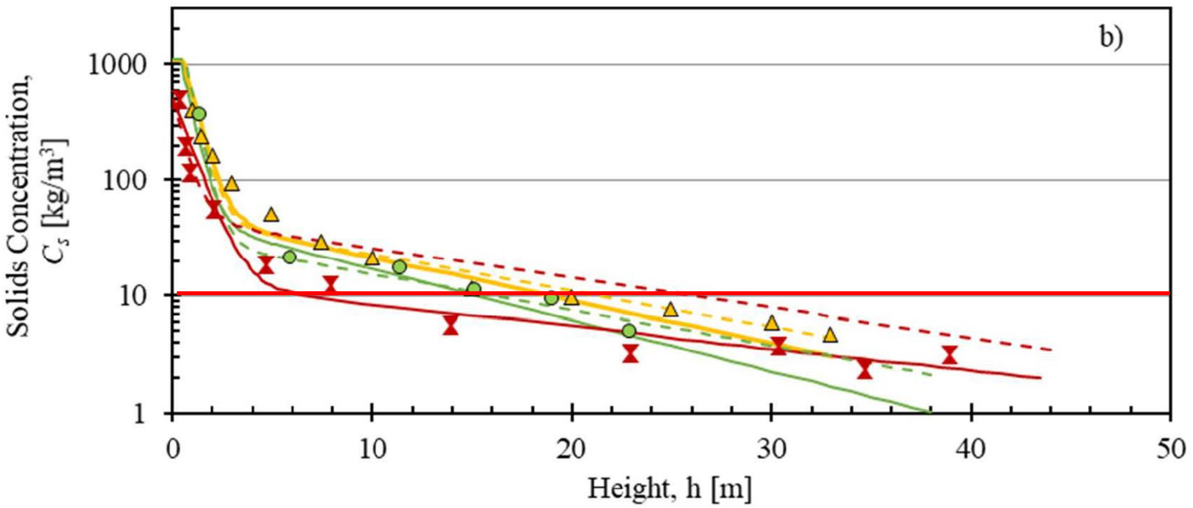
If $(u_0 - u_s) = 4\ m/s$

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



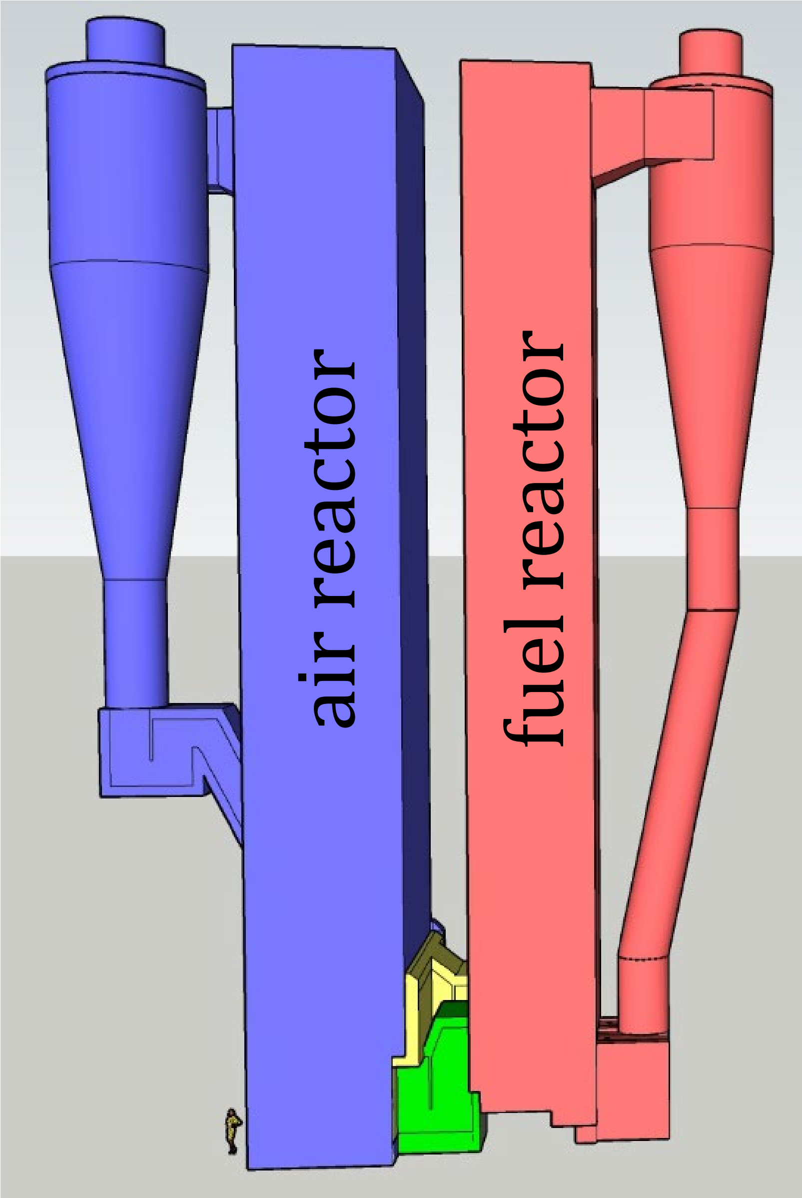


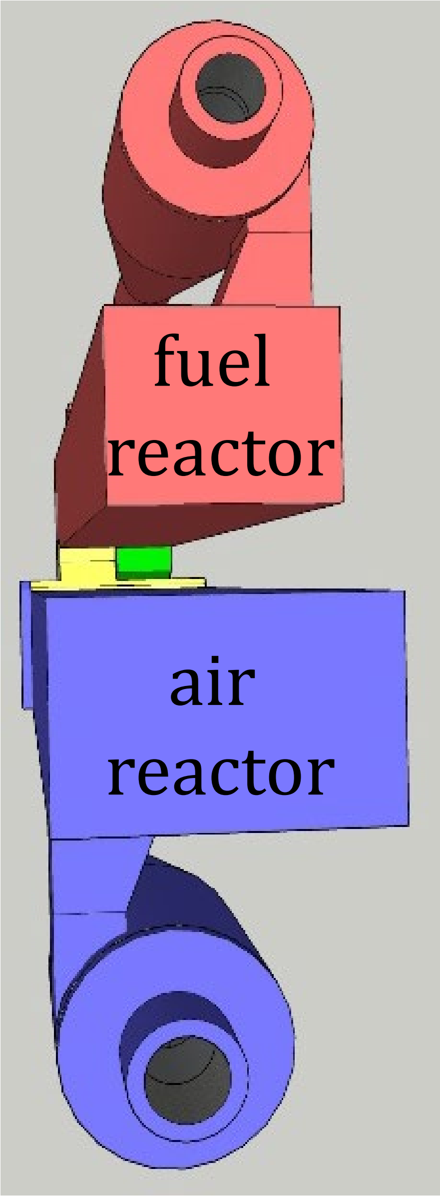
Solids concentration versus height. Data from two CFB boilers



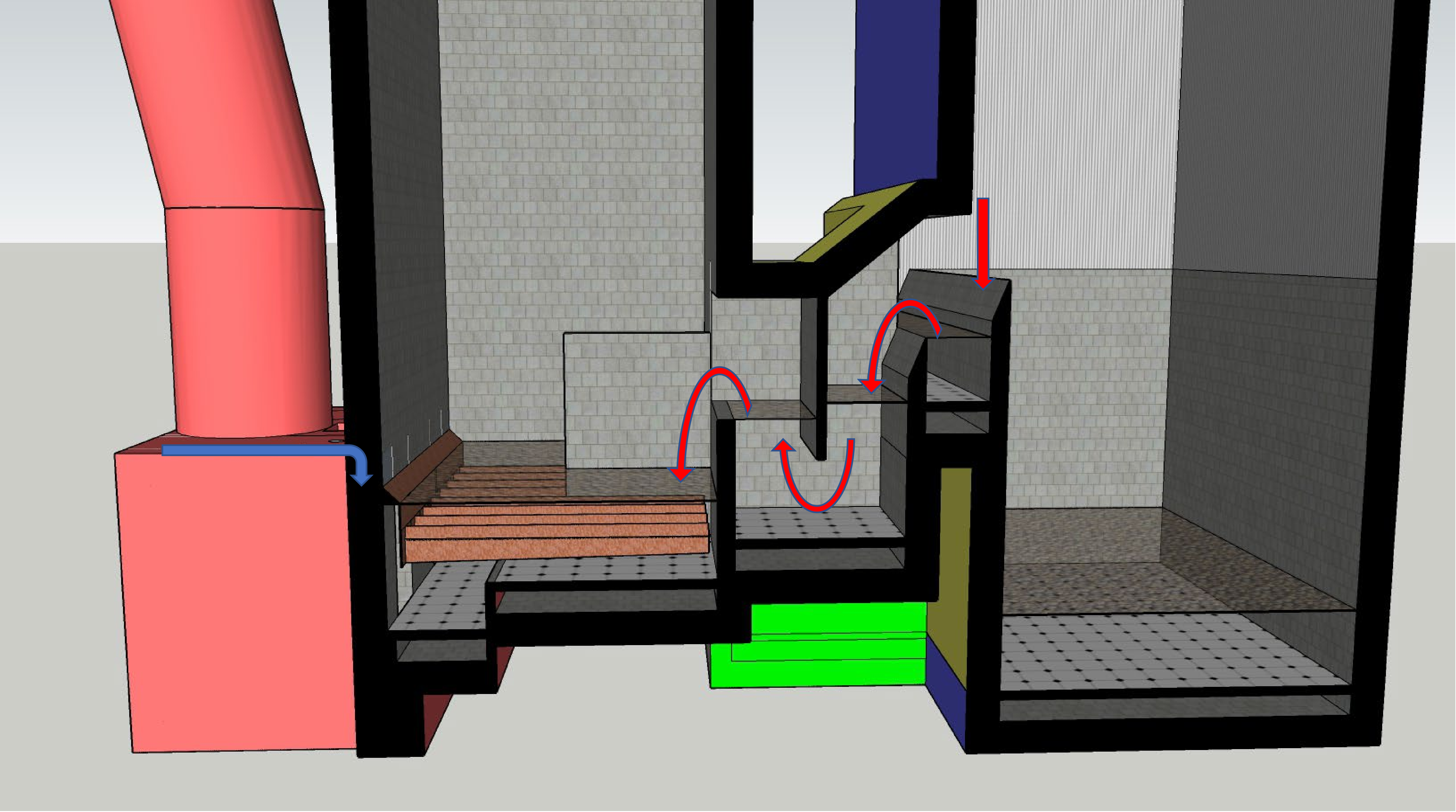
Solids concentration versus height for 3 CFB boilers. ▲ Emile Huchet, ● Zibo, ⧗ Turow.

200 MW CLC-CFB boiler, 40 m high

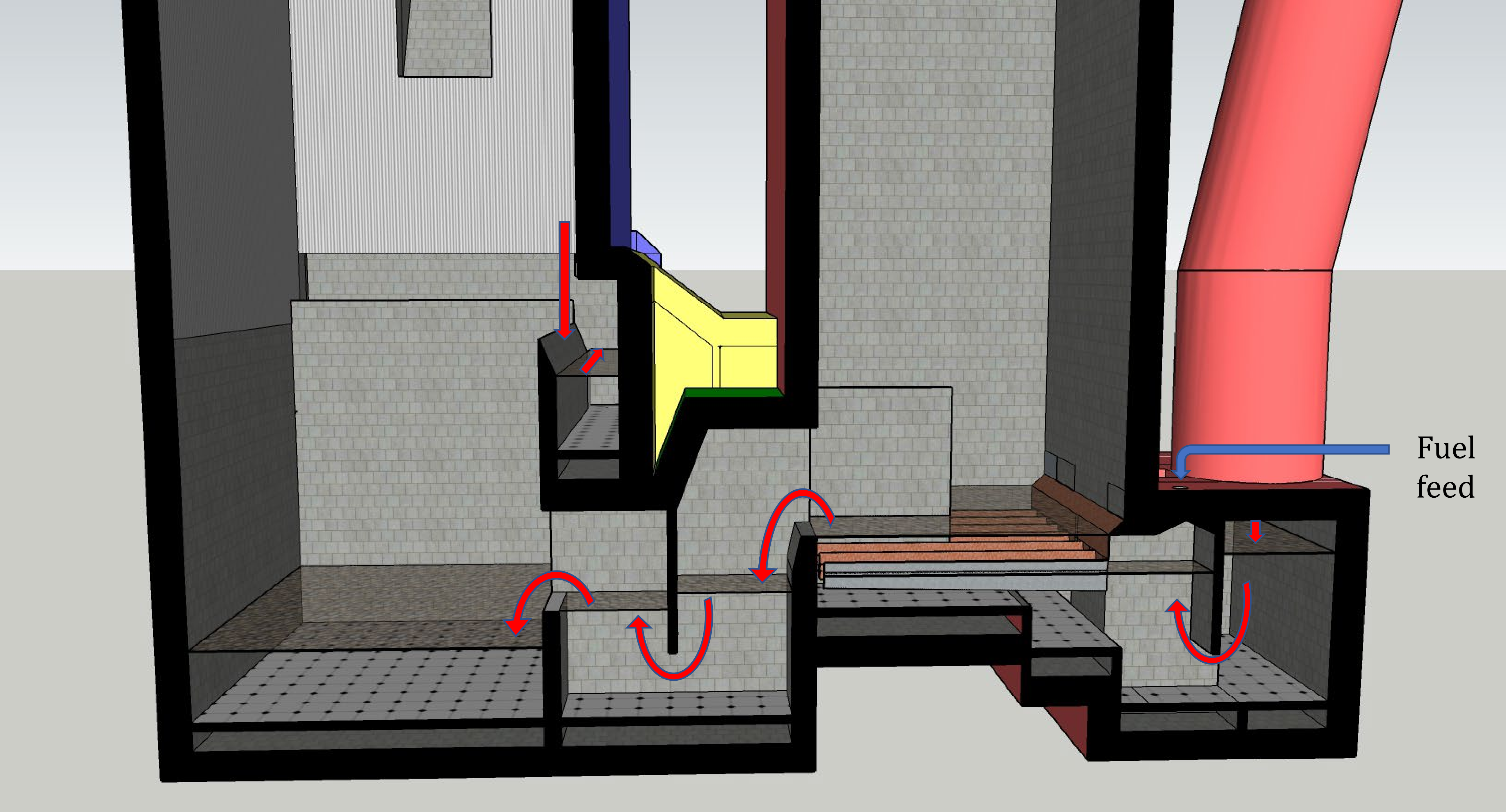




Lyngfelt, A., Pallarés, D., Linderholm, C., Lind, F., Thunman, H., and Leckner, B., Achieving Adequate Circulation in Chemical-Looping Combustion – Design Proposal for a 200 MW_{th} CLC Boiler, *Energy & Fuels* 36:17 (2022) 9588–9615

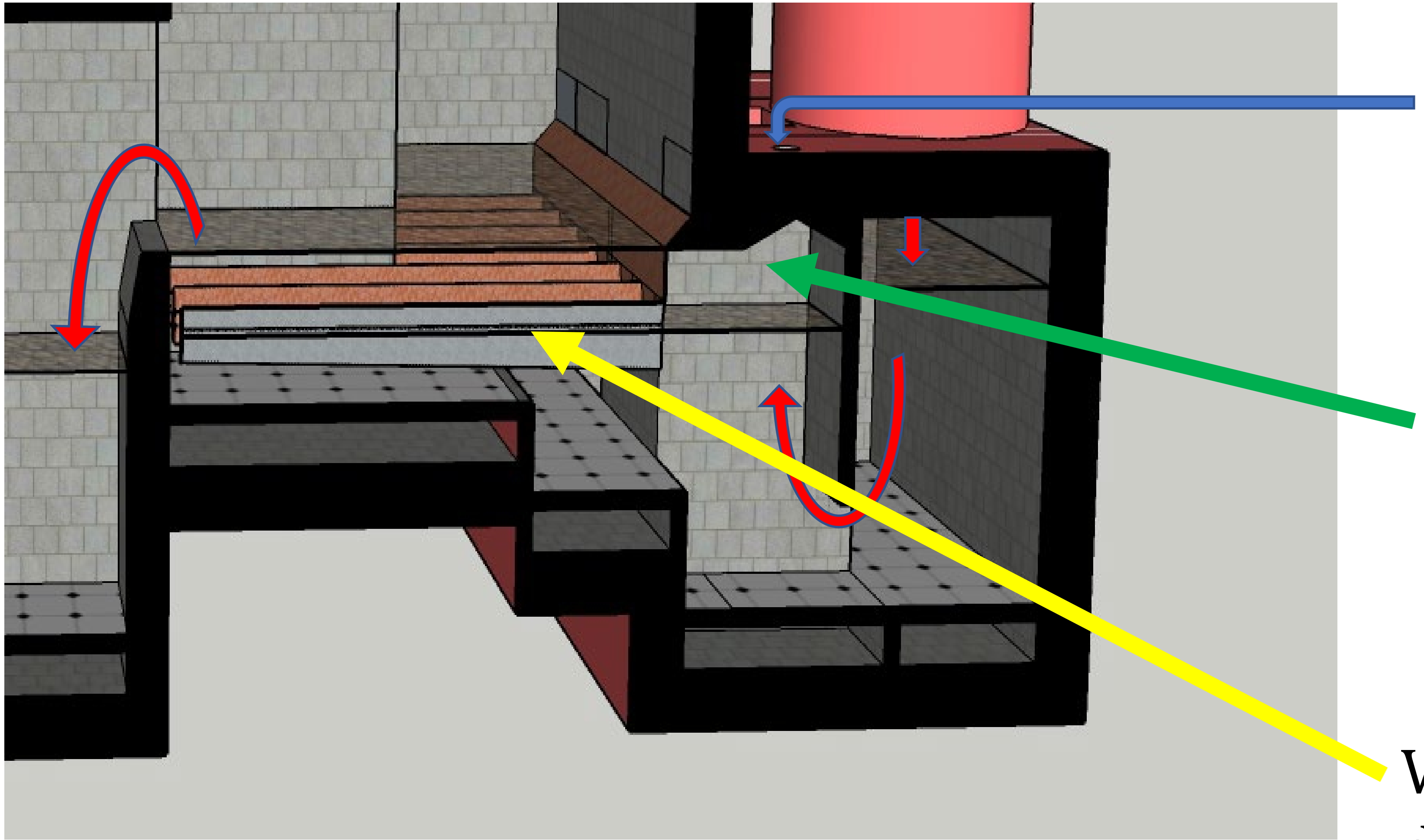


fuel reactor air reactor



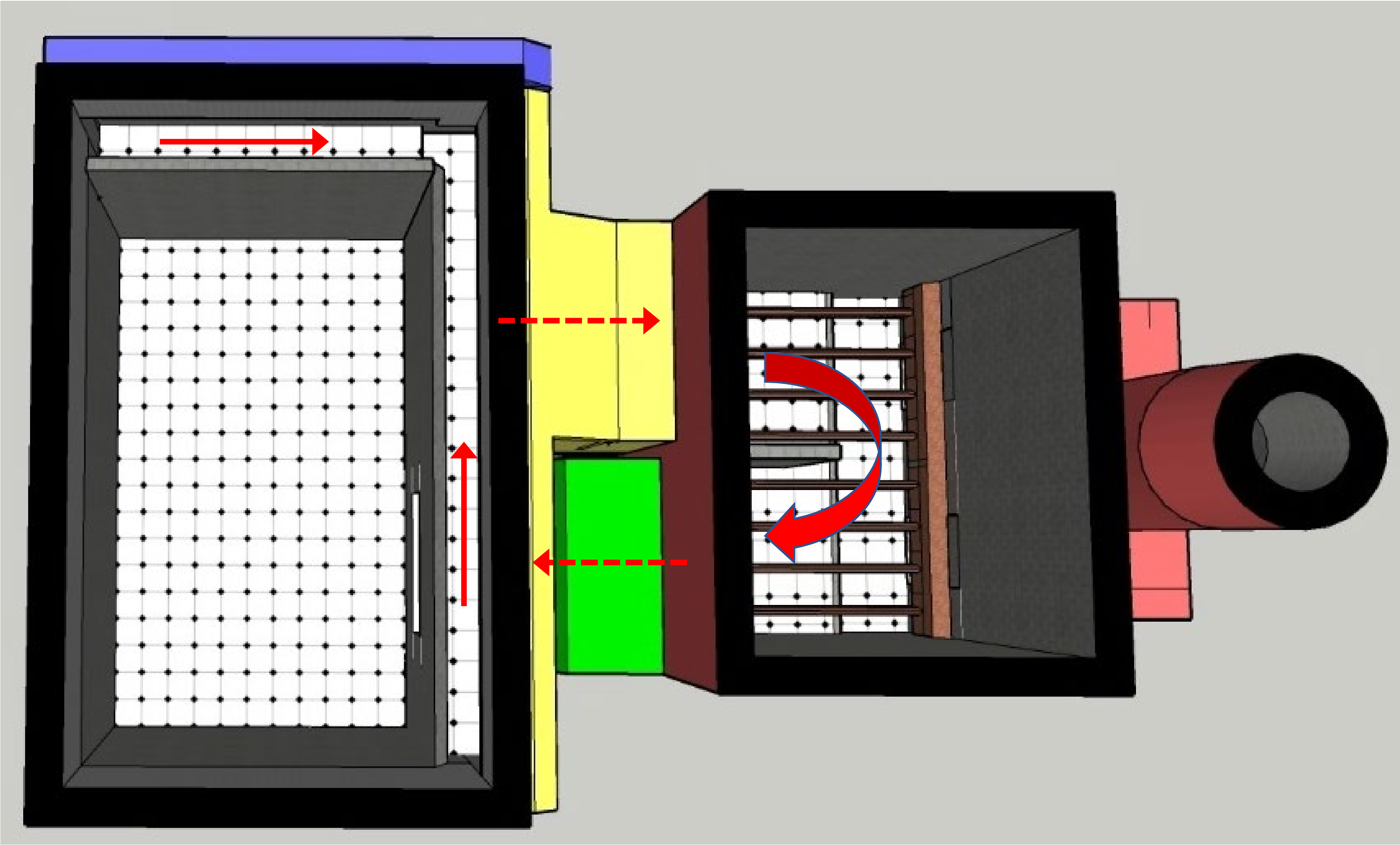
air reactor fuel reactor

fuel reactor

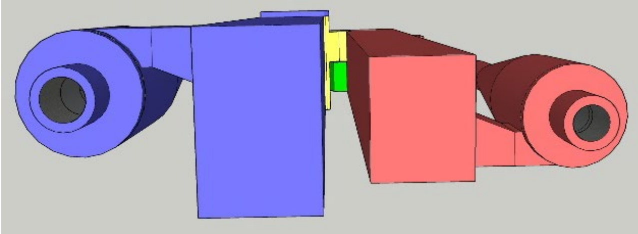


Xiaoyun Li, Session 6B, ”…. Volatiles Distributor …..

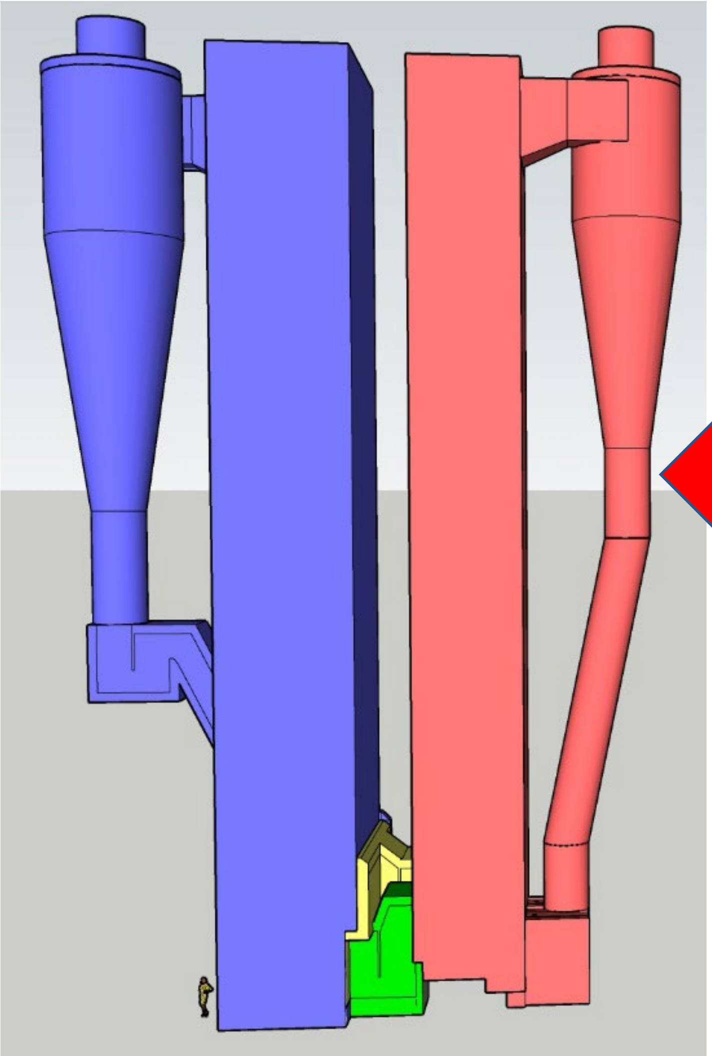
Xiaoyun Li, Anders Lyngfelt, Carl Linderholm , Bo Leckner, Tobias Mattisson, Performance of a volatiles distributor equipped with internal baffles under different fluidization regimes, *Powder Technology* 409 (2022) 117807

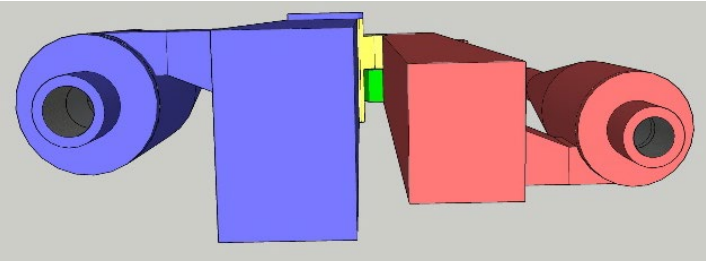


air
reactor



fuel
reactor





200 MW CLC-CFB, added cost for FR:

1500 m^2 insulated wall
at
2000 €/m^2

>>> 3 M€

or

0.3 M€/year

capture: 0.4 Mt CO_2/year

cost of fuel reactor : **0.75 €/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
<u>Total</u>	<u>20</u>	<u>15.9-25.8</u>	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

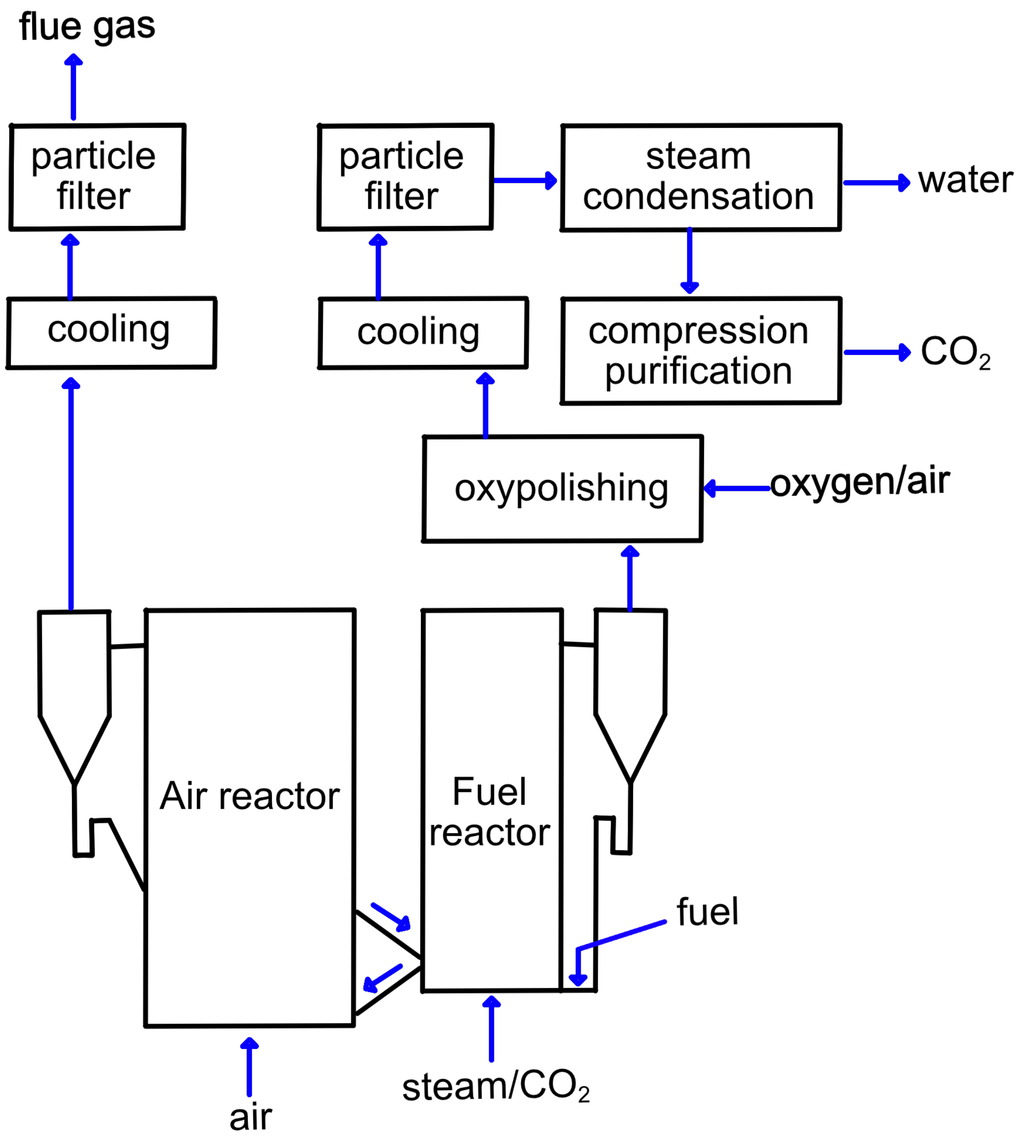


Table 2. Required purity of CO_2. [69, 70]

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

3a) conventional Selective Catalytic NOx Reduction.

- High reduction not possible
- Incoming NO needs to be low

3b) 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

3c) Addition of Cl_2O, to the co-removal system

- Deeper reduction possible
- Not commercial technology

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

Session 4A: Downstream Gas Treatment ....

Lyngfelt, A., Klas Andersson and Laura Raud Pettersson, Design of circulation system and downstream gas treatment of a full-scale boiler for Chemical-Looping Combustion
16th International Conference on Greenhouse Gas Control Technologies (GHGT-16), 23rd -27th October 2022, Lyon, France

Low NO from FR critical to avoid energy intensive distillation. What do we know?

Equilibrium NO concentration in a fuel reactor is well below 1 ppm.

Fuel-N reacting with oxygen carrier is only possible source

Operation with coal and ilmenite showed 1000-2000 ppm in 100 kW

Coal and ilmenite in 1 MW pilot showed 0 ppm

Unpublished data from 100 kW operation with biomass, showed 20-50 ppm of NO

Lyngfelt, A., Hedayati, A., Augustsson, E., Fate of NO and Ammonia in Chemical-Looping Combustion – Investigation in a 300 W CLC Reactor System, *Energy & Fuels* 36:17 (2022) 9628–9647

Addition of NO or NH_3 to the fuel reactor (with fuel/inert) of a 300 W pilot shows (for ilmenite):

In presence of fuel,
NO is completely reduced to N_2
No NH_3 is oxidized to NO

With no fuel and fully oxidized oxygen carrier:
NO is not reduced
Some NH_3 is oxidized to NO

With no fuel and partly reduced oxygen carrier:
NO is completely reduced to N_2
No NH_3 is oxidized to NO

=>There is good reason to assume that in a high riser, any NO formed would be reduced.

With a manganese ore and at moderate fuel flows:
NO is partly reduced
Some NH_3 is oxidized to NO

Fate of NO and Ammonia in Chemical-Looping Combustion – Investigation in a 300 W CLC Reactor System, Lyngfelt, Hedayati and Augustsson, *Energy & Fuels* 36:17 (2022) 9628–9647

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

Biomass:

- Eliminate/reduce emissions of NO_x
- Eliminate/reduce problems with alkali ash components

Steam Methane Reforming with CLC

- Potential for lower cost than conventional SMR without CO_2 capture

Thank you!