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CLC, a promising concept with challenging development issues

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TOTAL

IFP Energies nouvelles

Agenda

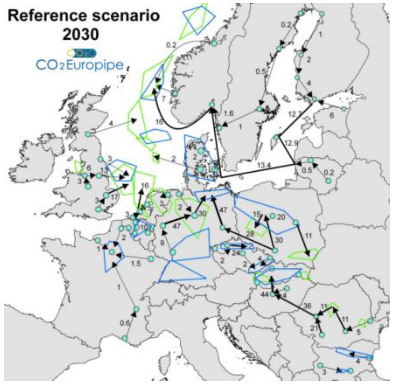
- CCS : **C**O_2 **C**apture and **S**torage
- CLC status
  - *Concept*
  - *Economics*
  - *Materials*
  - *Pilot plant testing*
- CLC technology and scale-up issues for solid fuels
  - *CLC scales for coal power plants*
  - *Fuel reactor concept*
  - *Control of solid circulation*
  - *Control of PSD*
  - *Attrition procedures for oxygen carrier screening*
  - *Limit ΔP in the Air Reactor to minimize energy penalty*
- Concluding Remarks

CO_2 Capture and Storage status

- **2° C Scenario** → Avoid 7 Gt by 2050 (50% from coal power plants)
  - 2016 : 15 CCS projects in operation : 28 Mt CO2 captured

this is about 0.4% of the « 2° C target » !!

- **Capture** : pre-combustion, post combustion, *oxycombustion*
  - Large additional investment , energy penalty
- **Transport** by boat or pipeline (≈1 M€/m(ϕ) /km (L))
  - Infrastructures are not there yet –permitting issue
- **Storage** in aquifers, oil and gas reservoir, coal beds
  - Storage capacity estimates are very encouraging
  - Public acceptance can be a challenge



- **CCS is a cost with no benefit (except for EOR projects or CO_2 use)**

CO2 storage cost *15 €/tCO2 (1 Mt/an) / 5 €/tCO2 (10 Mt/an)*
CO2 capture cost *> 30-40 €/t CO2 avoided*
CO2 transport cost *> 1- 3 €/t CO2 avoided*

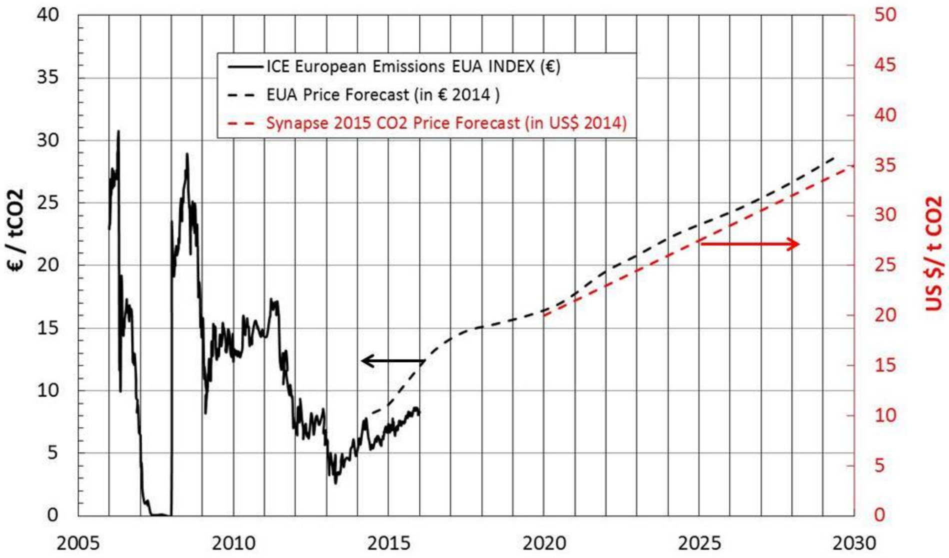
CCS =45-70 €/t CO2

*Ref: Technology roadmap CCS , IEA **(2013)*** *Ref Global CCS Institute: The status of CCS, Summary report **(2015)***

CO2 market / policy

- Huge investments will happen only with strong CO2 market perspectives
- There are encouraging signs …
  - Regional strategies (China, US, EU, Japan…)
  - Recent global COP 21 Consensus reached in Paris

but only 12% of CO2 emissions under local market regulations yet

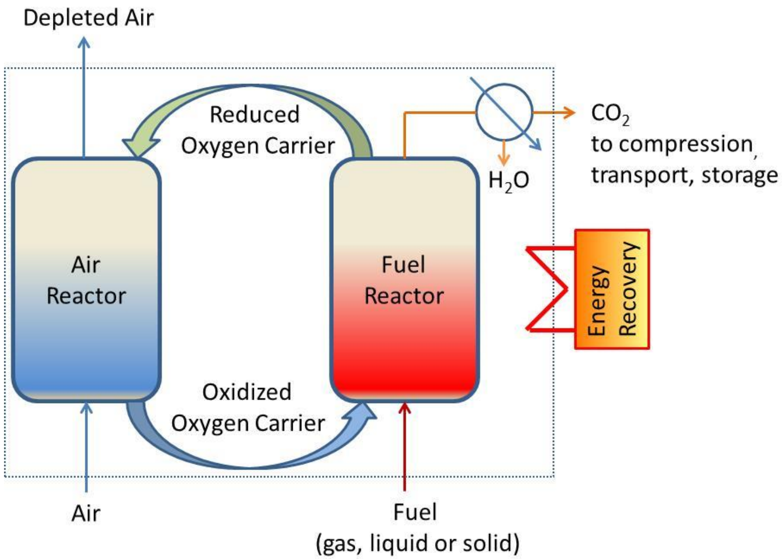


Reaching consensus takes time
A time to market delay of 10 -15 years is expected for CCS

Chemical Looping Combustion concept

- **CLC for CCS applications first proposed by Ishida (1987, 1994)**

Ref: *Fan et al., AIChE J, **(2015)** 61, 1-22* *Adanez et al., Progress in Energy and combustion Science **(2012)**, 38, 2, 215-282*



$$Me_xO_{y-1} + 1/2\ O_2 \rightarrow Me_xO_y$$

$$2(n+m)Me_xO_y + C_nH_{2m} \rightarrow (2n+m)Me_xO_{y-1} + nCO_2 + mH_2O$$

- **Benefits**
  - Low energy penalty
    (5% with 4% related to CO2 compression cost)
  - Low CO2 avoidance cost
    our estimate 37€/t CO2

	Reference CFB unit	Amine MEA30%	CLC
Net Electric production (MWe)	630	630	630
Net Electric yield (%)	44.9	34.9	40
Coal consumption (t/h)	198	255	222
Capex (M€)	1215	2064	1785
Opex (M€)	156	220	206
Cost of Electricity (€/MWh)	63	98	88
CO2 avoidance cost [€/t/CO2)		53	37

Impacts of CCS
for a 630 MWe Coal power plant
IFPEN Total study (basis= France 2012)

A promising G2 concept to be demonstrated

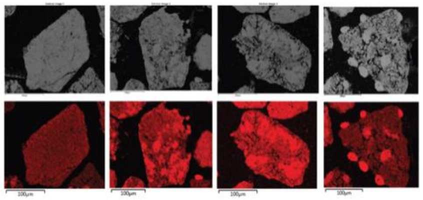
CLC material : oxygen carrier

- **Several potential oxygen carrier materials (hundreds evaluated already)**
  - Metal oxydes : Ni, Fe, Mn, Co, Cu (…) , perovskites ….
- **Several points to consider**

  Oxygen transfer capacity, Reactivity, Aging , Availability, syn.materials or mining ores ?

	Mining Ore	**Synthetic material**
Process	grinding / sieving	spray drying / granulation granulation
Price	0.15 (crude) → 1 €/kg prepared	in the range of 10 €/kg
Recycling	back to the ore industry ?	Treatment (hydro/pyrometallurgy? 3-5 €/kg)
Shape	low sphericity	high sphericity

- **Redox aging is the issue**
  - **No report of successfull operation > 500 cycles**
  - Relates to ionic migration and volume changes (Fan, 2015)



Ilmenite in Chalmer's 100kW$_{th}$ pilot plant
(Knutsson et al, (2014)

- **Industrial perspective =15000–30000 cycles per year**
  - **Impact of aging on process economics is significant**

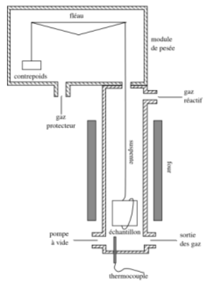
We need to improve oxygen carrier aging performance

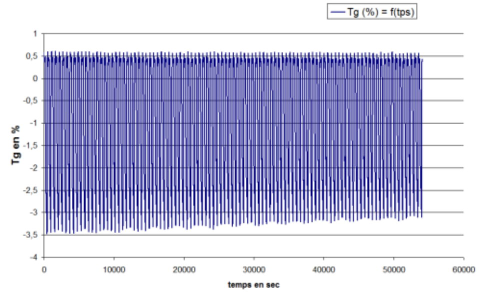
*Ref: Fan et al., AIChE J, **(2015)** 61, 1-22 Knutsson and Linderholm, 3rd International Conference on CLC, Chalmers **(2014)**,*

CLC tools for testing

Chemical reactivity

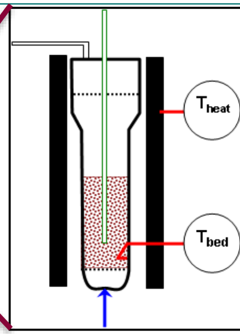
TGA (20 mg)

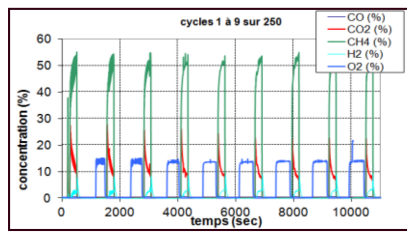




Reactivity In fluidized bed

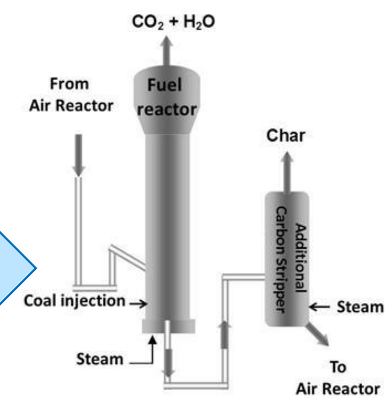
Batch (200 g)



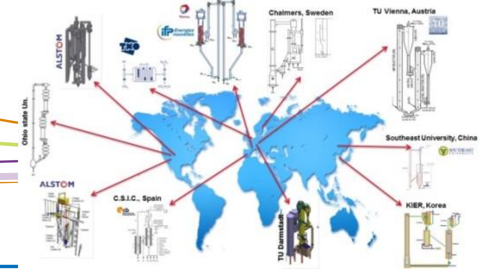


10 kW pilot plant
CH4, CO, coal, pet coke continuous combustion

Continuous pilot plant (35 kg)



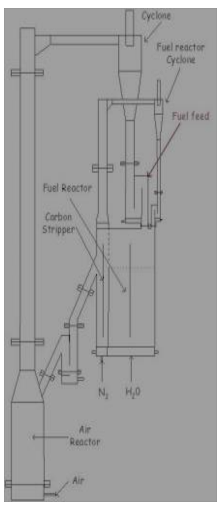
- Nature of the feedstock greatly impacts design aspects
- For solid fuels: gasification is a limiting step and fuel reactor design is critical



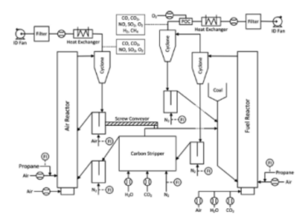
Several pilot plants all over the world

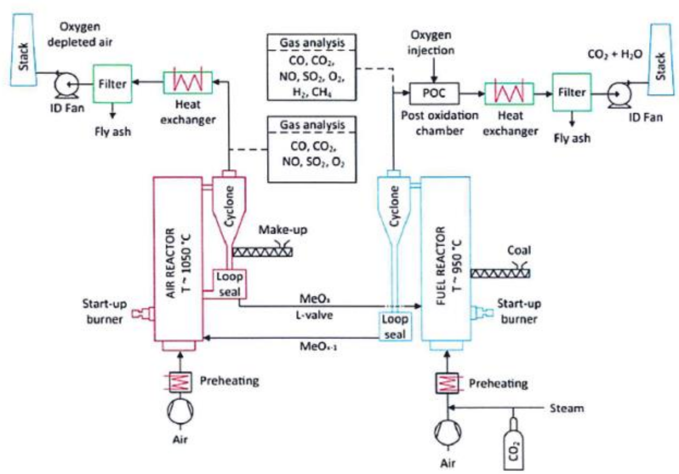
CLC continuous operation successfully achived (100-200 redox cycles max)
There is a need for optimisation of technology

Chalmers 10 kW and 100 kW



TU Darmstadt 1MW



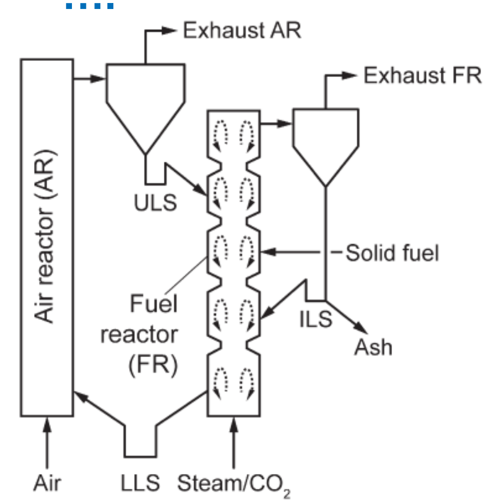


Combustion of volatile materials is an issue

Autothermal operation. Fuel Reactor design?

Investigation of new concepts

- Staged Fluidized bed (TU Hamburg)
- CFB fuel reactor with internals (TU Vienna)
- ….

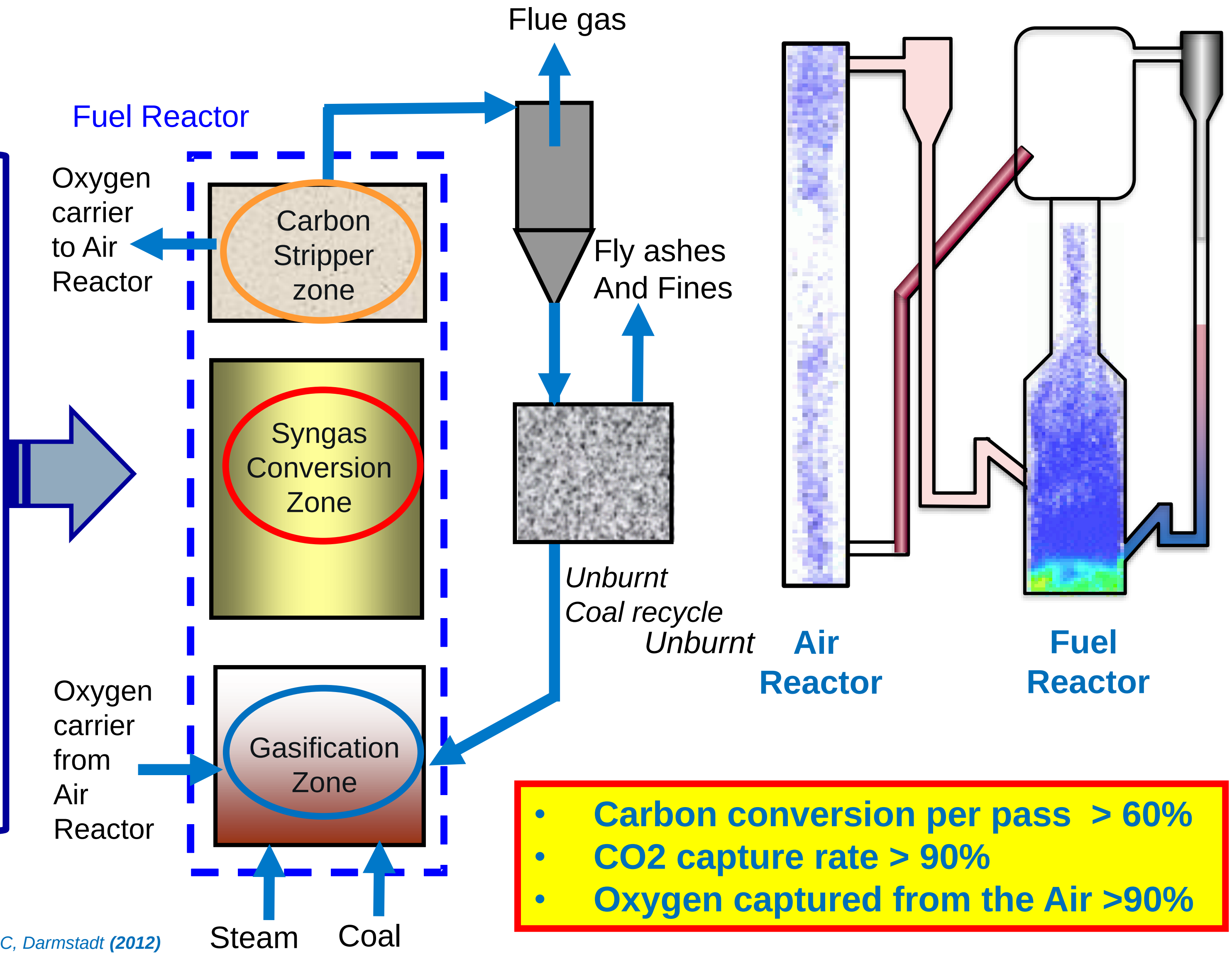


*Ref: Berguerand et al., Fuel, **(2008)**, 87, 2713-2726, Lyngfelt and Linderholm, Energy Procedia **(2014)** 63, 98-112, Strohle et al., Applied energy **(2014)**, 113, 1490-1495
Ohlemuller et al., J. of Energy Ressources and Technology **(2016)** 138, 1-7 Guio-Perez et al., CERD, **(2014)** 92, 1107-1118, Thon et al., 2nd Int; conference on CLC , Darmstadt, **(2012)***

Ifpen-Total CLC process concepts

Process constraints

- to maximize CO_2 capture (*coal application*)
- enough contact for syngas and volatiles combustion
- enough time for gasification reaction (*coal application*)

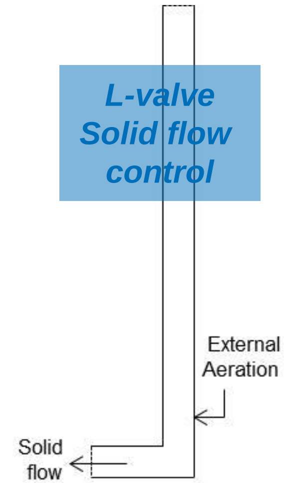


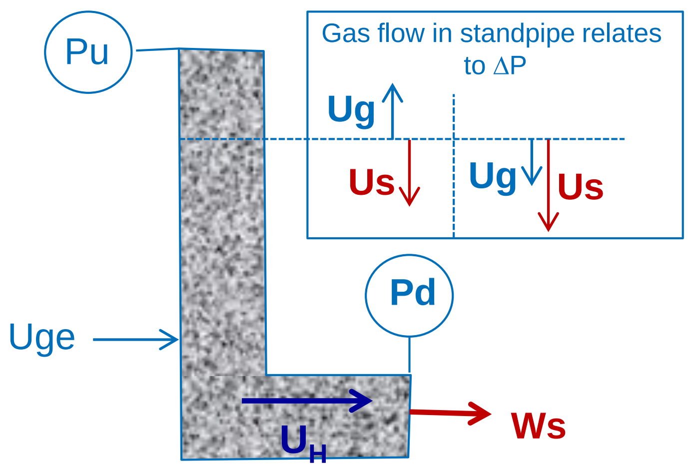
- **Carbon conversion per pass > 60%**
- **CO2 capture rate > 90%**
- **Oxygen captured from the Air >90%**

Ref: Bourgeon et al., 2nd Int.Conf CLC, Darmstadt ***(2012)***

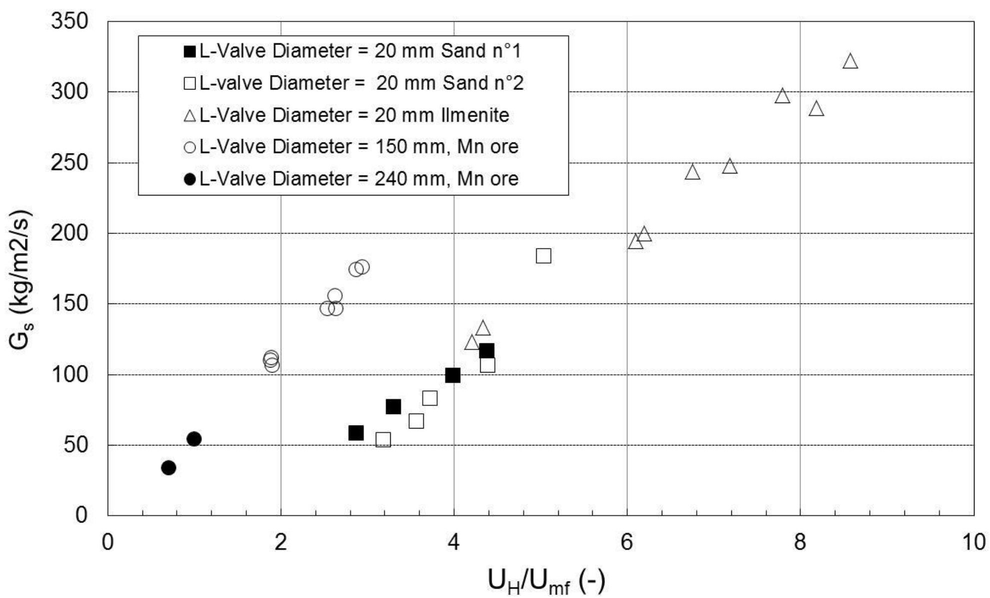
Control of solid circulation

- **Large flowrates in between interconnected reactors**
  - → Control of temperature / oxygen carrier reduction rate
- **CLC is high temperature > 850° C**
  - Not suitable for mechanical valves (FCC Slide valves…)
    - →Use of non mechanical L-valves
    - →Use group B material oxygen carrier





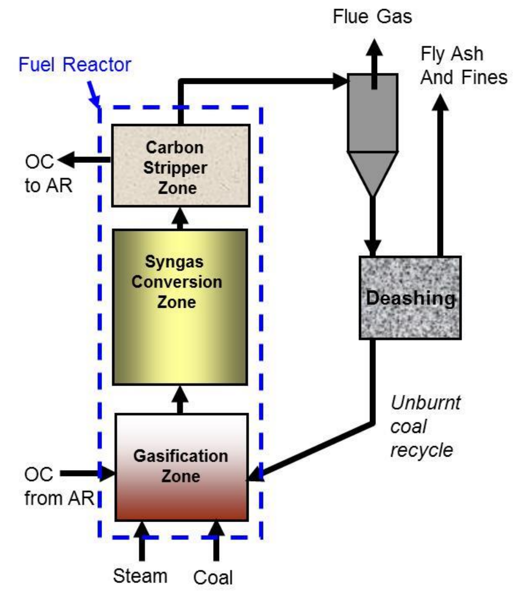
Solid flow relates to actual gas flow in the valve

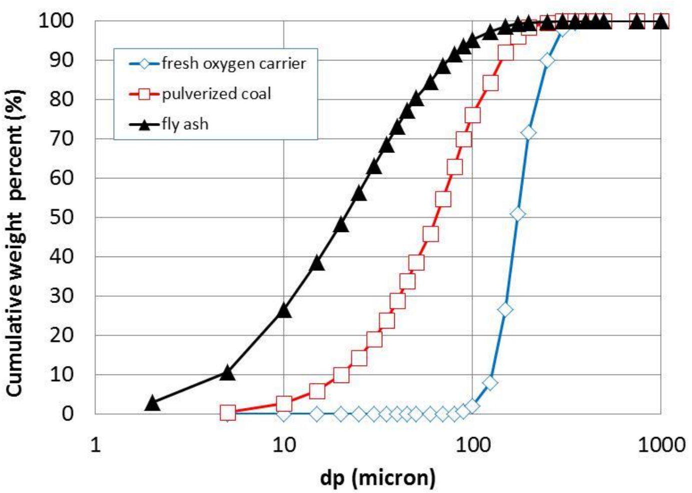


Ref: Knowlton and Hirsan, Hydrocarbon Processing ***(1978)*** *27, 149-156 Yazdanpanah et al., Powder Technol.* ***(2012),*** *221, 236-244*

Control of PSD : 3 different solids to consider

- **Oxygen carrier** (100–300 microns – design choice)
  Large PSD (L–Valve, carbon stripper separation)
- **Coal** (50–100 microns – design choice)
  Small PSD (Fast gasification, carbon stripper separation)
  → high efficiency cyclones to keep char in the FR
- **Ash**
  - **Fly Ash** (0–100 microns –no choice)
    Avoid accumulation in the unit (L–valve)
    Fly ash elutriation has to be considered
  - ***Agglomerated Ash ?*** *(depends from coal and $T_{Fuel\ reactor}$)*
    Relates to coal composition and T fuel reactor
    Avoid settling at the fuel reactor bottom



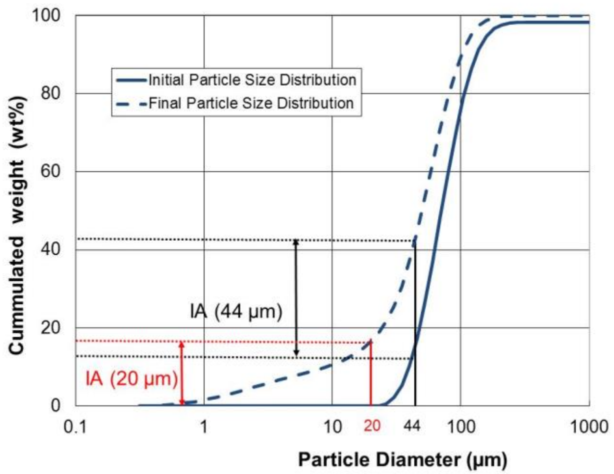


Account for PSD changes: - along the loop
- function of aging

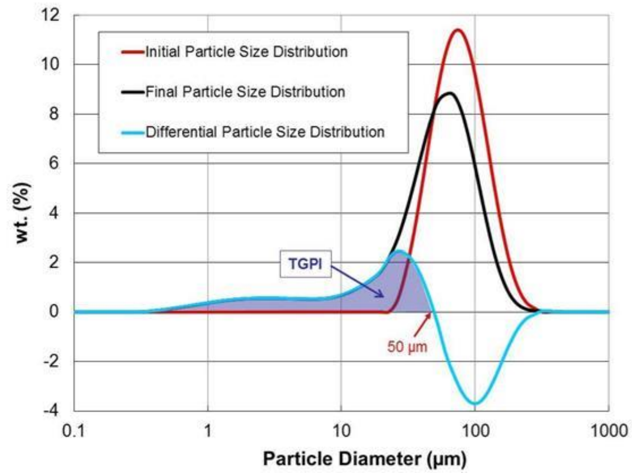
Attrition procedures for oxygen carrier screening

Screening → small samples available with different physical properties (d_{sv}, ρ_p)

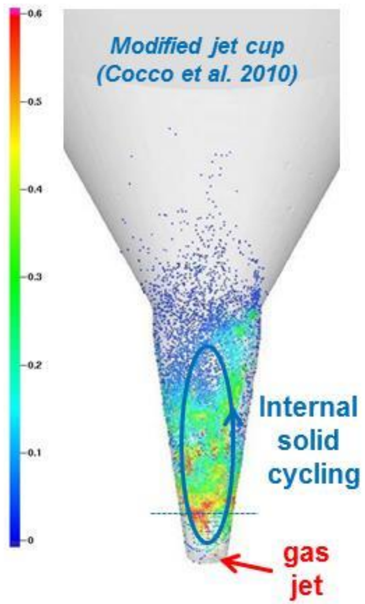
Challenge : use a workable attrition index
use comparable testing conditions
with similar stress



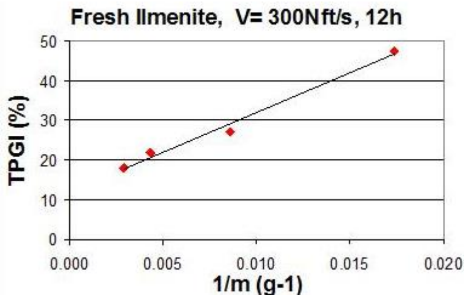
Group A particles



Group B particles



	AI(20) (wt%)	AI(44) (wt%)	TPGI (wt%)
Group A particles	15	26	27
Group B particles	3	5	15



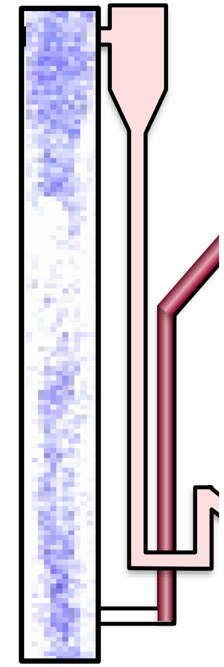
Ref: Cocco et al., Powder Technol. ***(2010)*** *200, 224-233* *Amblard et al. Powder Technol.* ***(2015)*** *274 455-465*

Minimize ΔP in the air reactor

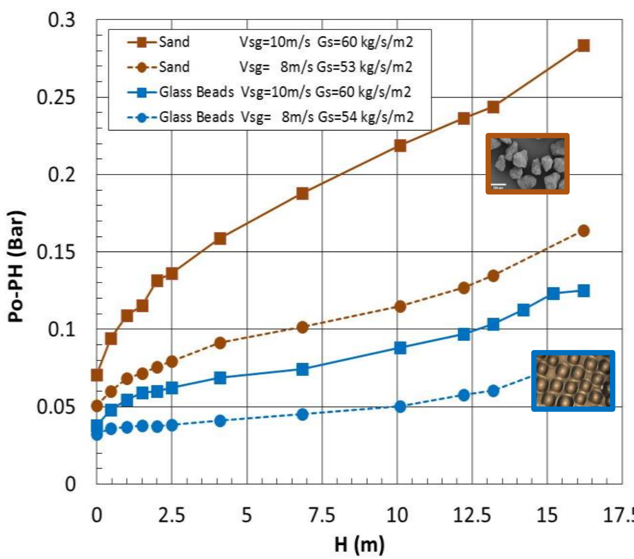
CLC energy penalty is strongly depending upon air compression:

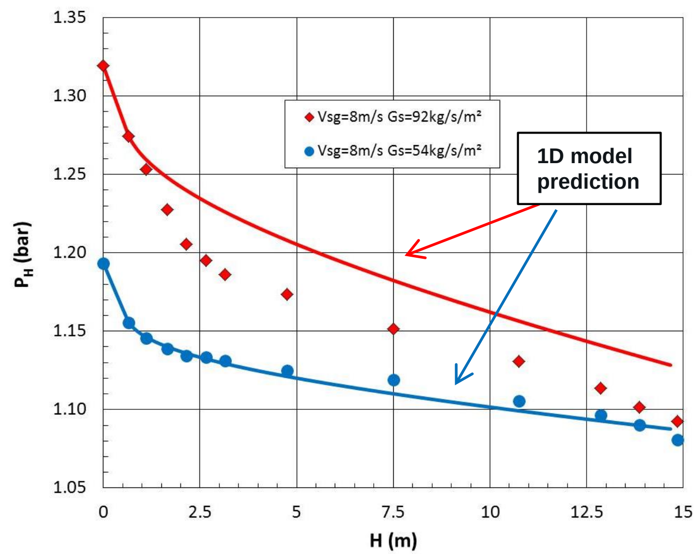
ΔP air reactor = 100 mb ⟺ 0.5% energy penalty

objective: find operating conditions that minimize ΔP in air reactor while maximizing air / oxygen carrier contact



RISER D=0.3m | **Data collection** → **Modelling**





Strong unexpected impact of particle shape !

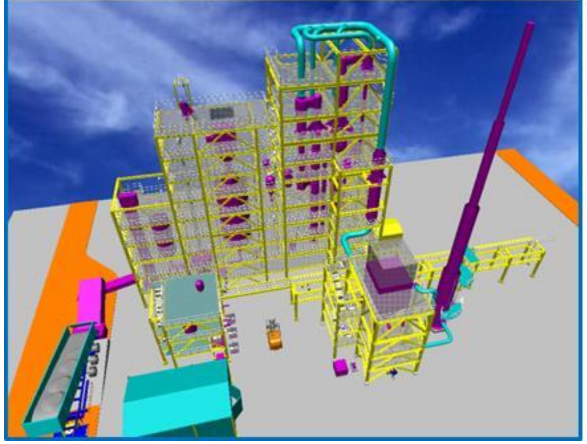
1D : Drag adjustment needed
CFD : Difficulty to well predict Core annulus structure

Ref: Rodrigues S. et al., Powder Technol. ***(2015)*** *272, 300-308* *Rodrigues S. et al., Powder Technol.* ***(2015)*** *283, 519-529*

Conclusions

- **CLC is a promising G2 concept for CCS**
  - Favourable economics and limited energy penalty
  - Demonstrated at pilot scale with a limited number of redox cycles (<500)
- **Next step is demonstration:**
  - But aging of oxygen carrier is an important issue to be solved
  - Efforts needed for process optimization, scaling up and other aspects such as flexibility of operation
- **CLC future in the CCS perspective ?**
  - Demos are very expensive
    - We need a clear CO_2 market perspective
  - Time to market delay to 2025–2030 for CCS ?
    - Opportunity to optimize oxygen carrier materials and technology

TOTAL IFPEN Declic 3MW demo project



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