

From Clean Combustion to CCU: intriguing topics for process engineering and materials scientists

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Numbers

Napoli, Torino, Ferrara

98 Tenured researcher

58 Administrative and technical staff



Outline

- Intro: the fossil fuel lean and fuel rich scenarios
- Capture ready combustion: Oxycombustion and CLC
- CO₂ capture: CaL, Capture with fine powders
- CCU: methanation; Met-OH production; enzymatic CCU
- CCU and solar energy: *Solar aided CaL; Thermochemical splitting of CO₂*



CCUS is one of the pillars of global energy transitions, together with renewables-based electrification, bioenergy and hydrogen

Why?

Energy Agency (IEA) *Energy Technology Perspectives 2020*

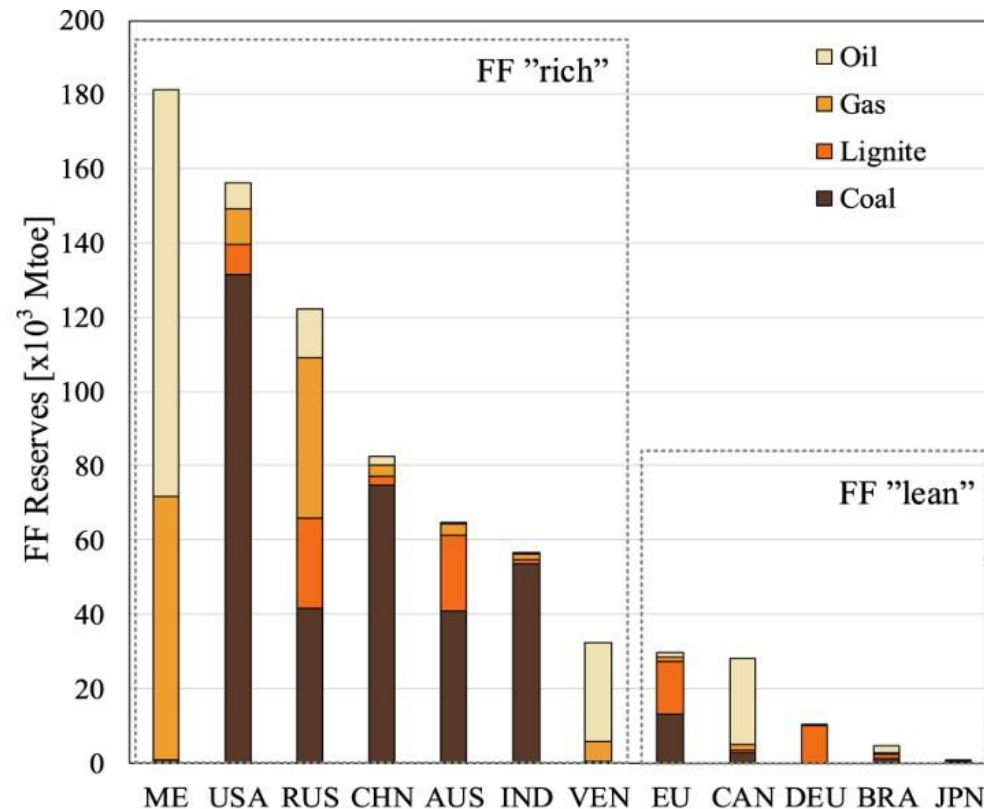


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Two trends:

The fossil fuel **rich** vs the fossil **lean** countries



The threat to climate change mitigation posed by the abundance of fossil fuels,
[Filip Johnsson](http://orcid.org/0000-0003-3106-5379) <http://orcid.org/0000-0003-3106-5379>

Fossil fuel **lean** countries

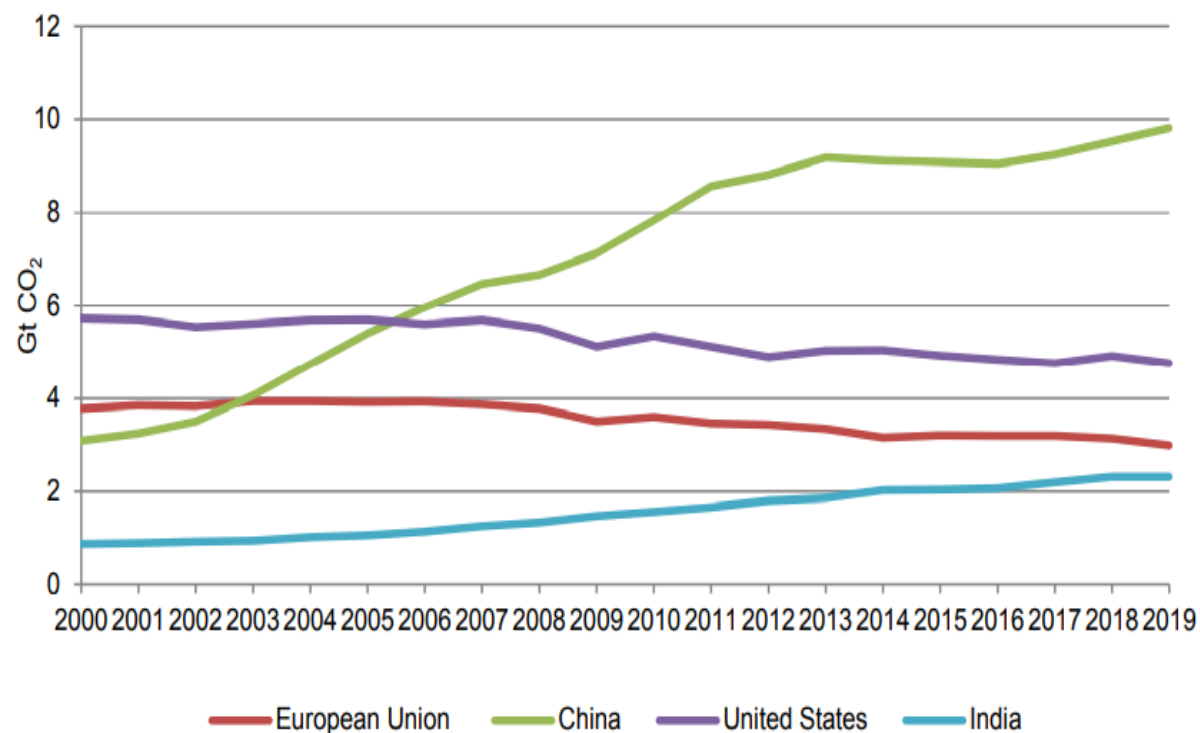
...are facing a remarkable increase of renewable energy but---

- Moreover **fossil power** will still be needed to some extent **to balance the fluctuations** in Solar/wind power
- Carbon removal technologies are still required in **certain sectors**: steel, chemicals and cement, aviation, road freight and maritime shipping
- **BECCS** technologies can provide a means of removing CO₂ from the atmosphere, i.e. “negative emissions (eg. power station fueled with biomass and equipped with CCUS)
- The **use** of the CO₂ for an industrial purpose can provide a **potential revenue** stream (not only enhanced oil recovery, but also as feedstock for synthetic fuels, chemicals and building materials.

Fossil fuel **rich** countries...

...will not stop producing energy from fossil fuels neither easily nor shortly

CO₂ emissions from fuel combustion: trends for selected economies



Example: China

- Chinese coal-based power generation capacity doubled in less than 10 years
- Chinese coal-fired power plants are relatively new: 70% of installed capacity less than 10 years of age (power plant life time=40 years)
- CO₂ capture technology can be retrofitted to existing plants

China has stated, in its nationally determined contribution to the Paris Agreement, that it aims to peak GHG emissions in 2030

- Share of CCS in electricity generation of only 3% in 2030 for the USA, China, Japan and the European Union.
- Currently 37 projects of CCS

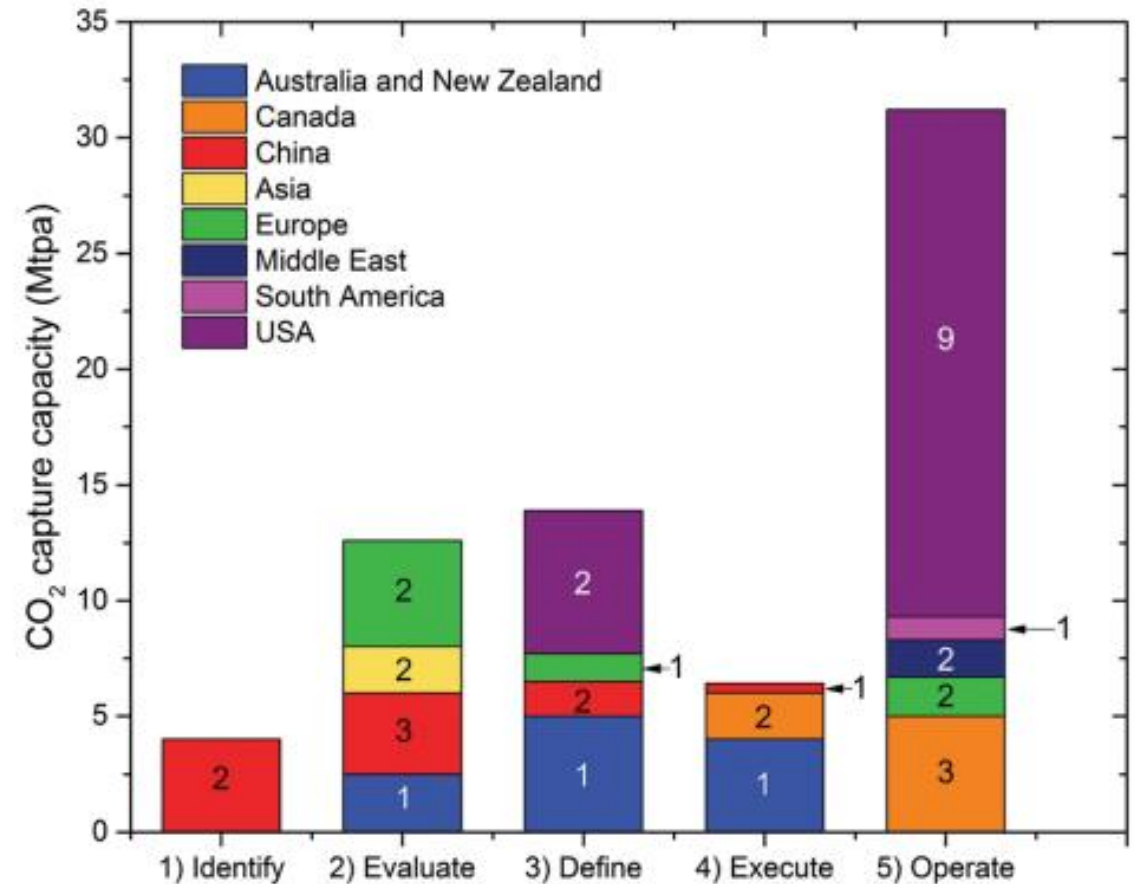
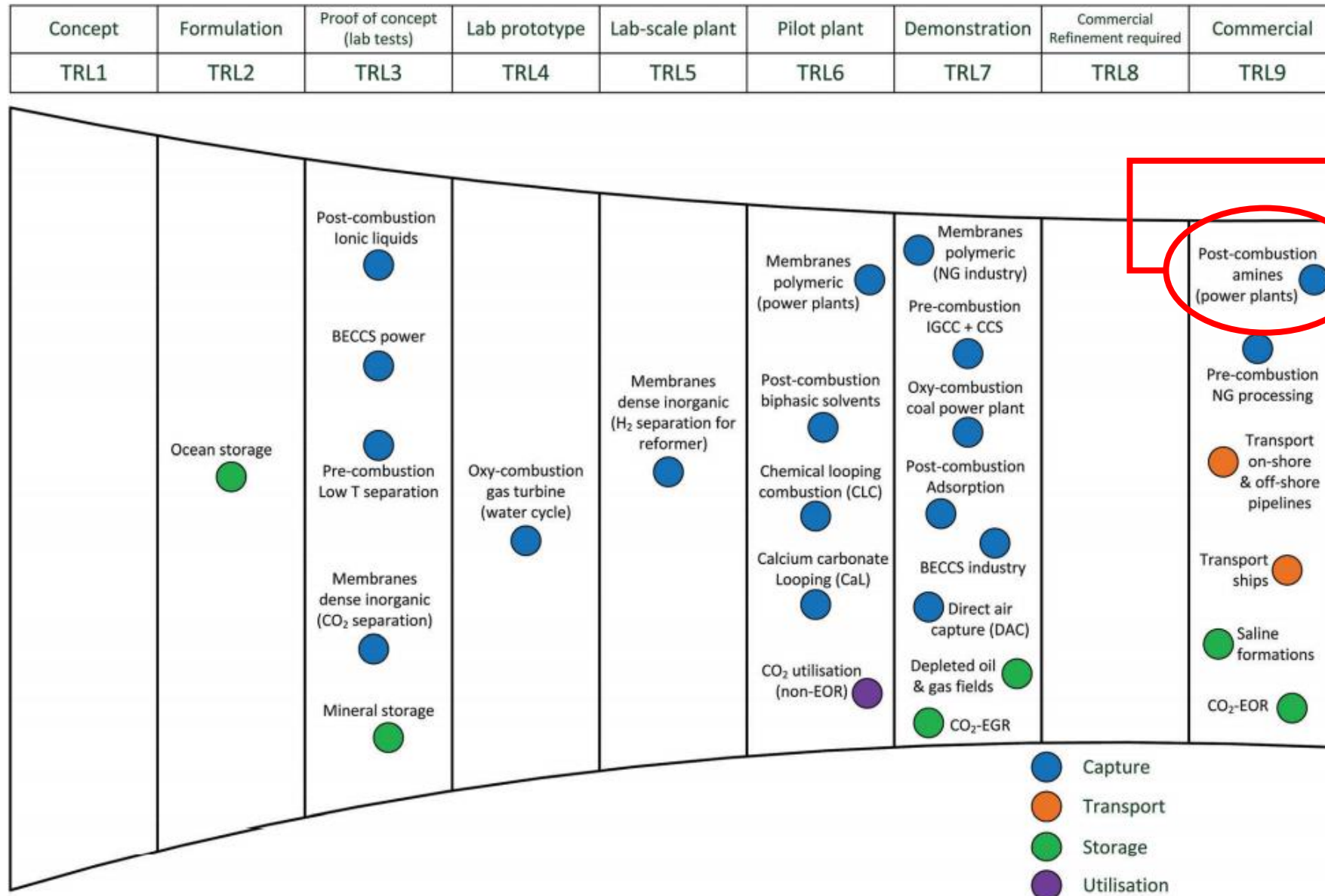


Fig. 2 The CO₂ capture capacity of commercial-scale CCS projects worldwide. The number labelled on each proportion of capture capacity corresponds to the number of projects. Data from the Global CCS Institute.⁴



energy intensive
CO₂ desorption
step: high cost

CO₂ capture cost
≈40 €/ton

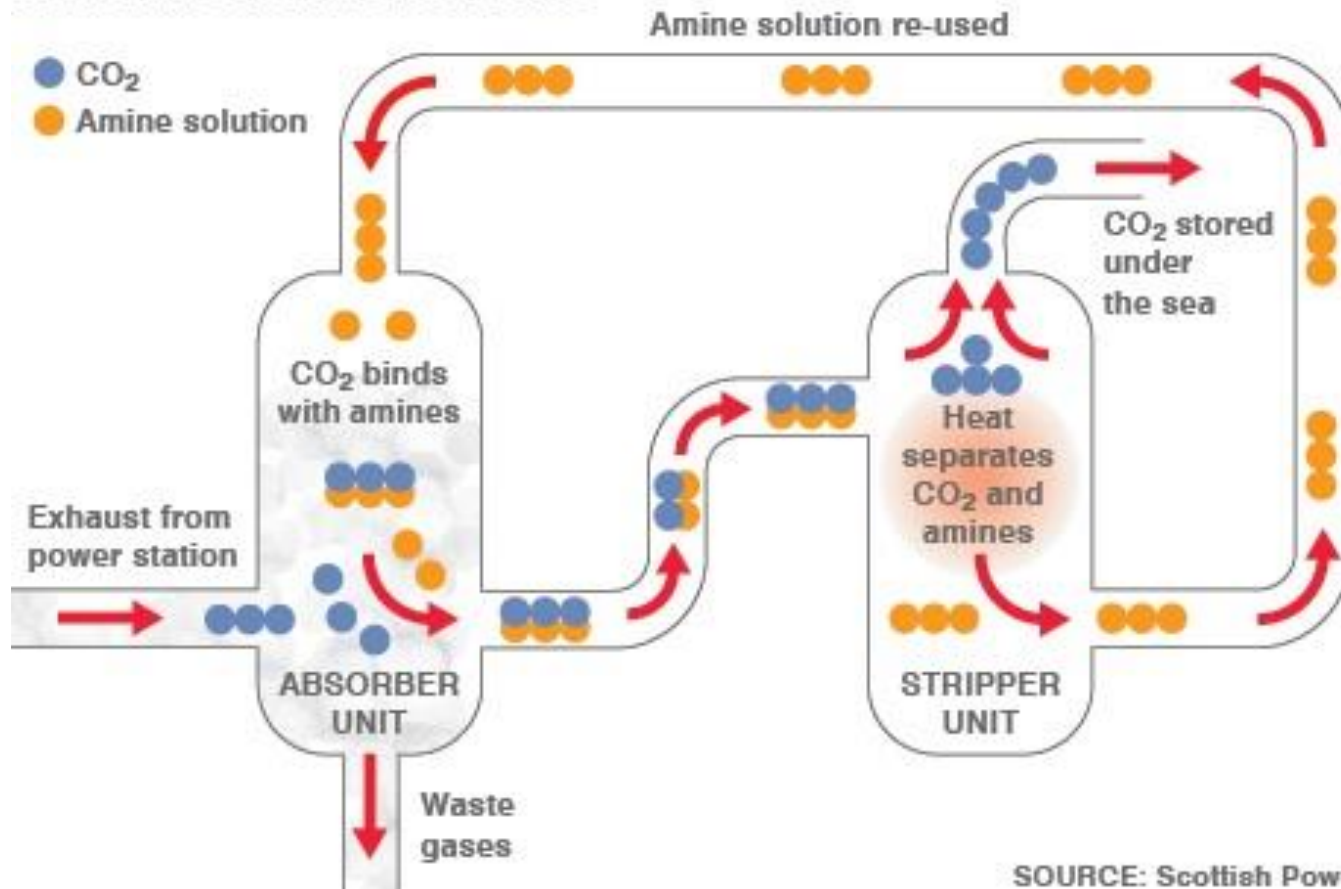
Fig. 1 Current development progress of carbon capture, storage and utilisation technologies in terms of technology readiness level (TRL). BECCS = bioenergy with CCS, IGCC = integrated gasification combined cycle, EGR = enhanced gas recovery, EOR = enhanced oil recovery, NG = natural gas. Note: CO₂ utilisation (non-EOR) reflects a wide range of technologies, most of which have been demonstrated conceptually at the lab scale. The list of

The current benchmark is chemical absorption with aqueous amine solutions (30 wt% MEA which was originally proposed in 1930).

Energy intensive CO₂ desorption step: high cost

- CO₂ capture cost ≈40 €/ton
- Up to 40% energy penalty

HOW CARBON CAPTURE WORKS

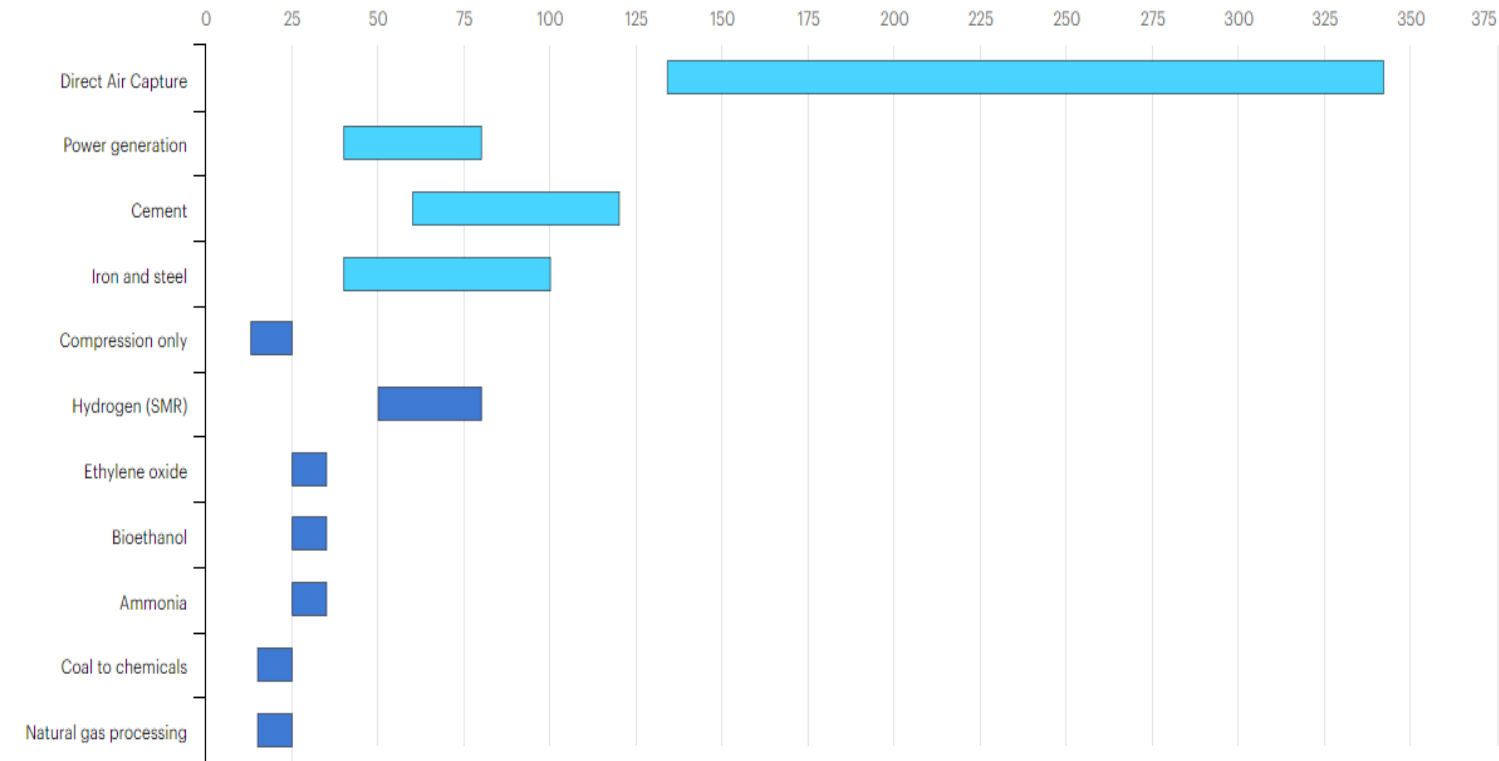


SOURCE: Scottish Power

The cost of CO₂ removal is high if CO₂ is diluted

Levelised cost of CO₂ capture by sector and initial CO₂ concentration, 2019

USD/tonne

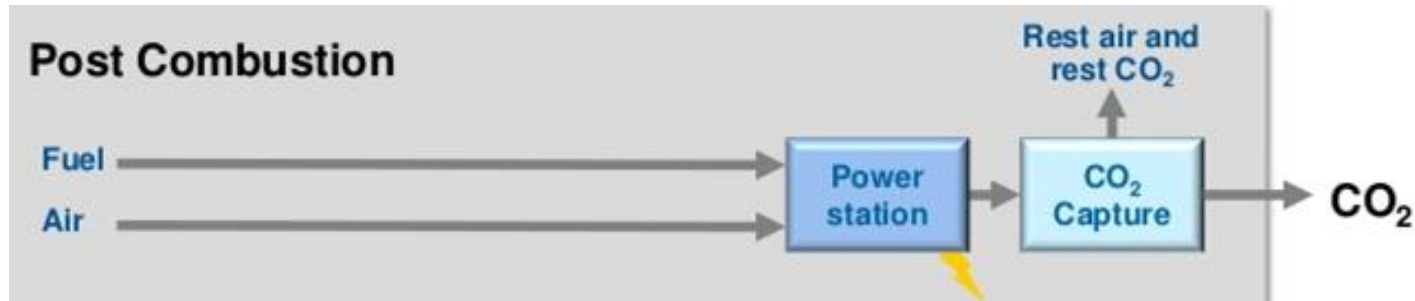


● Low CO₂ concentration

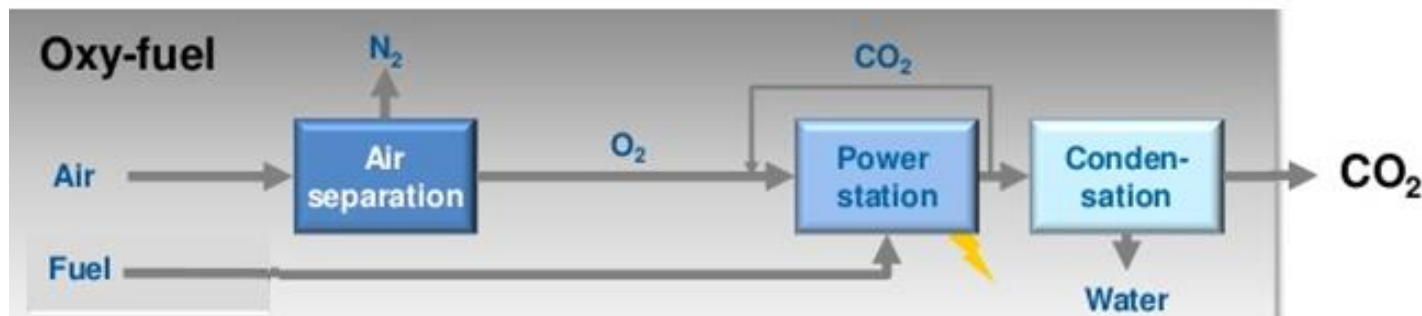
● High CO₂ concentration



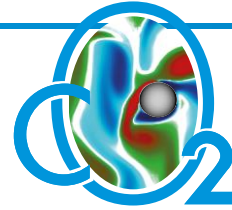
Capture ready combustion: oxycombustion



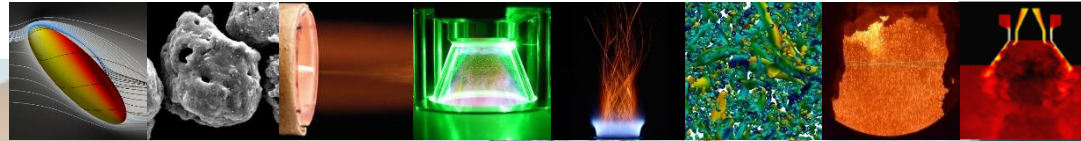
- Efficient and scalable
- Well suited for retrofit
- Well suited for BECCS



- Oxycombustion is a combustion process using **oxygen and recirculated flue gas**
- exhaust gas consists almost exclusively of CO₂



OXYFLAME



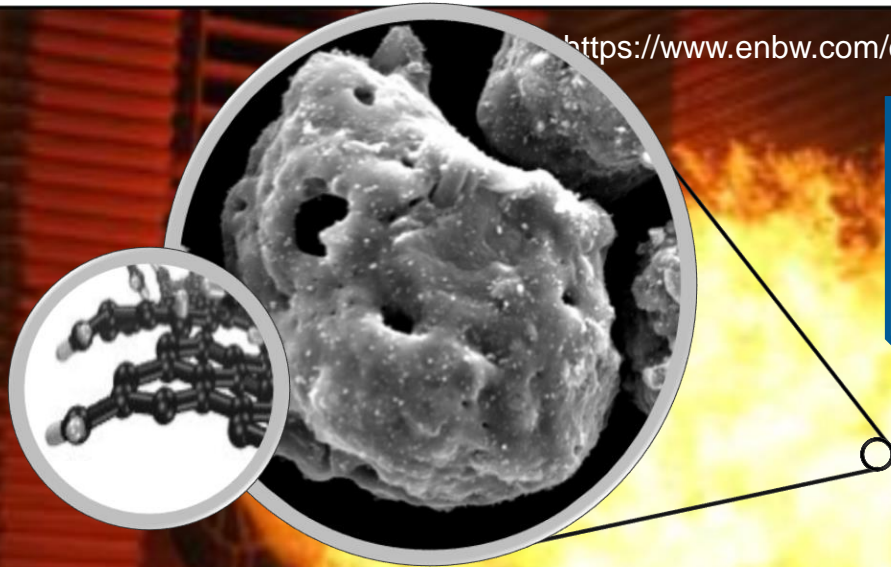
20 subprojects, 40 researchers, 12 years



https://www.enbw.com/company/the-group/energy-production/new-buildings-and-major-projects/karlsruhe_rheindampfkraftwerk/

Scales \Rightarrow CRC/TRR 129 structure

- 3 project areas



Scales involved?

Micro scale

- Atoms and particles
 - 10^{-10} – 10^{-4} m

Intermediate scale

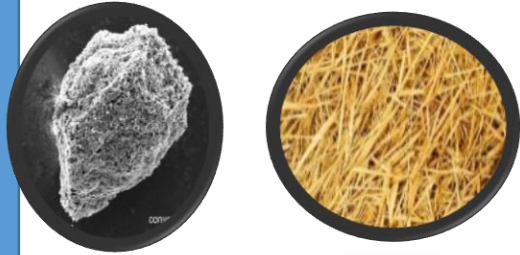
- Transport processes

Full scale

- Apparatus dimensions
 - 10^1 – 10^2 m

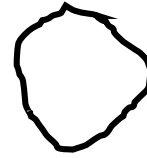
[ENBW]

Materials in Oxycombustion



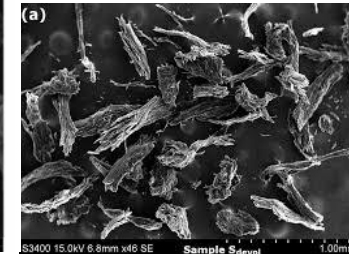
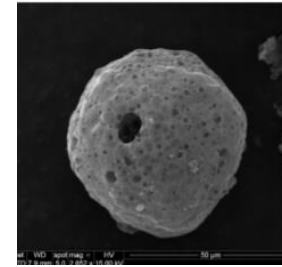
in a boiler

Fragmented or unfragmented char particle ?

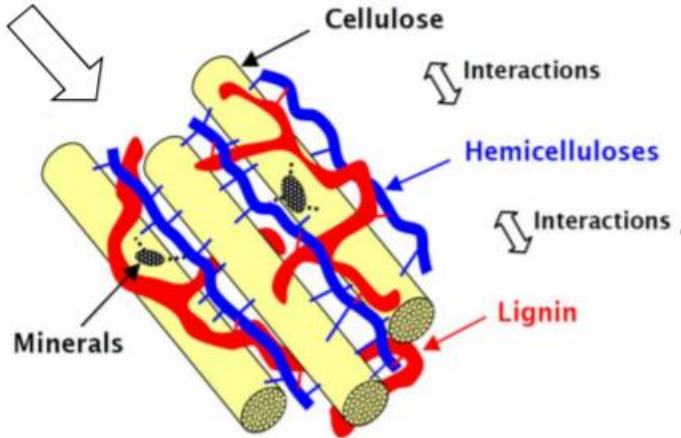


Model of fragmentation for thermal stress and internal pressure

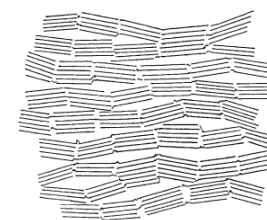
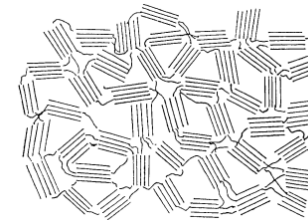
Spherical or elongated char; swollen or non swollen, porous? or not



Heat



Graphitized or disordered char ?



Model of thermal annealing

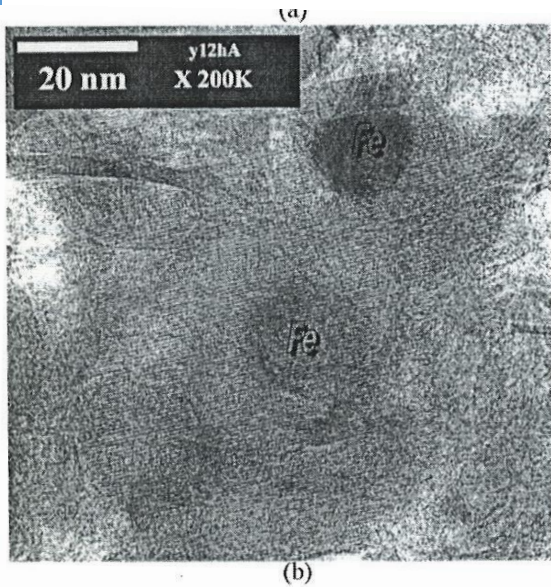
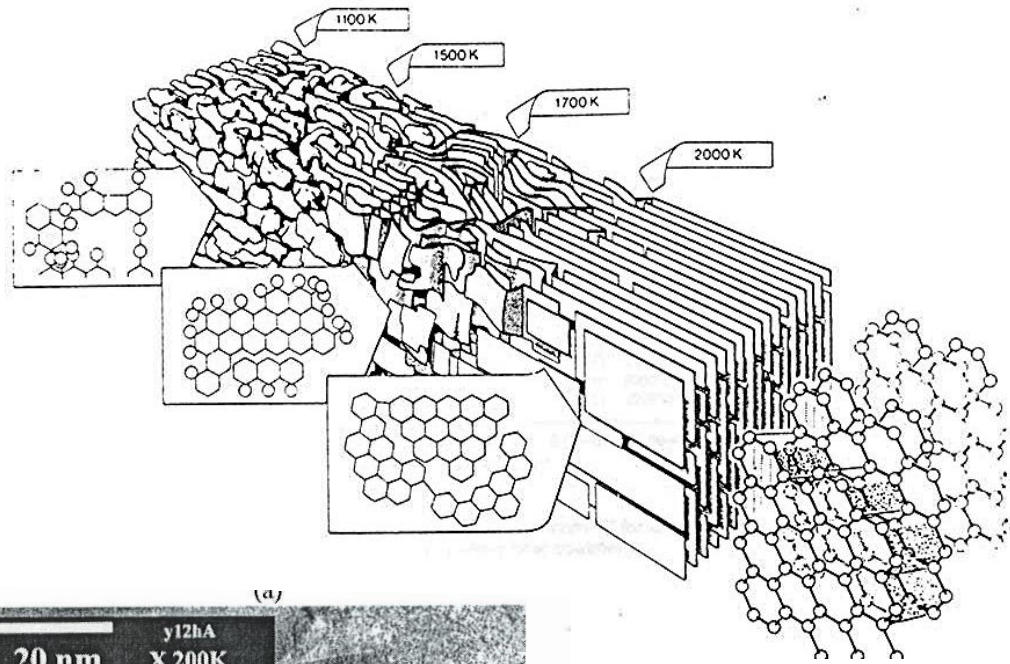
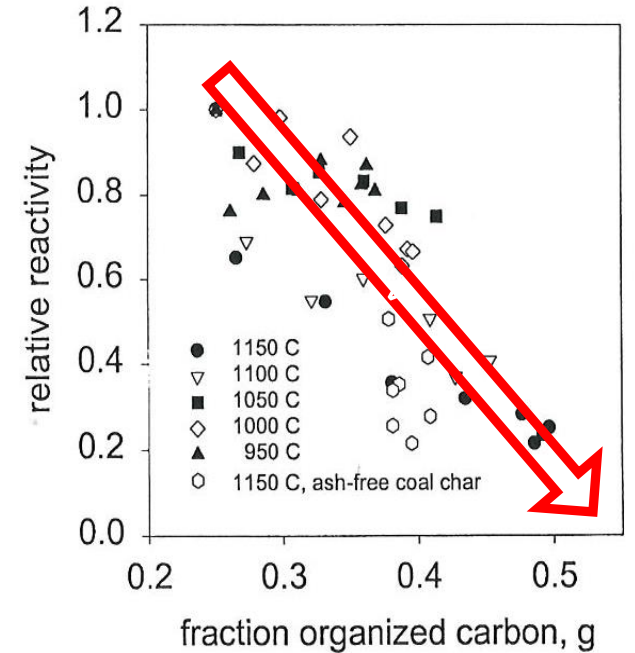
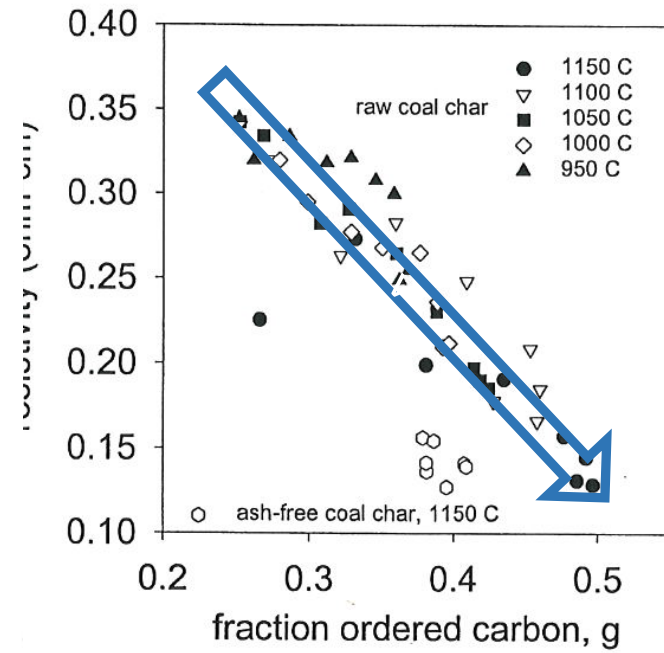


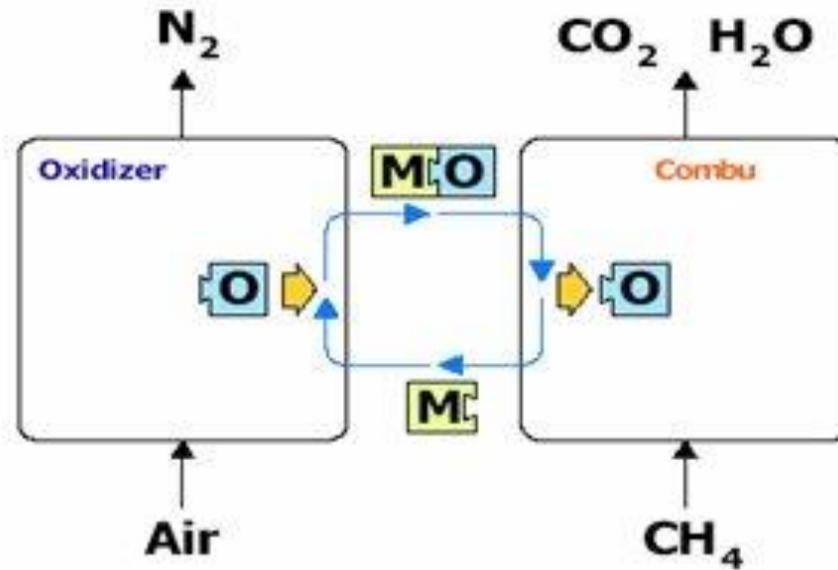
Fig. 4. High resolution transmission electron micrographs of the carbon structure around the iron particles for y12hA. (a) Micrograph showing many randomly oriented crystallites, (b) near-perfect crystallite structure around the iron particles.



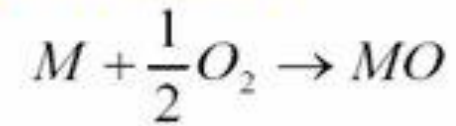
Graphitization:

- **reduces reactivity in boilers**
- **decreases resistivity of the material**

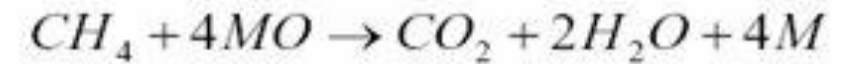
Capture ready combustion Chemical Looping Combustion (CLC) of liquid and gaseous fuels



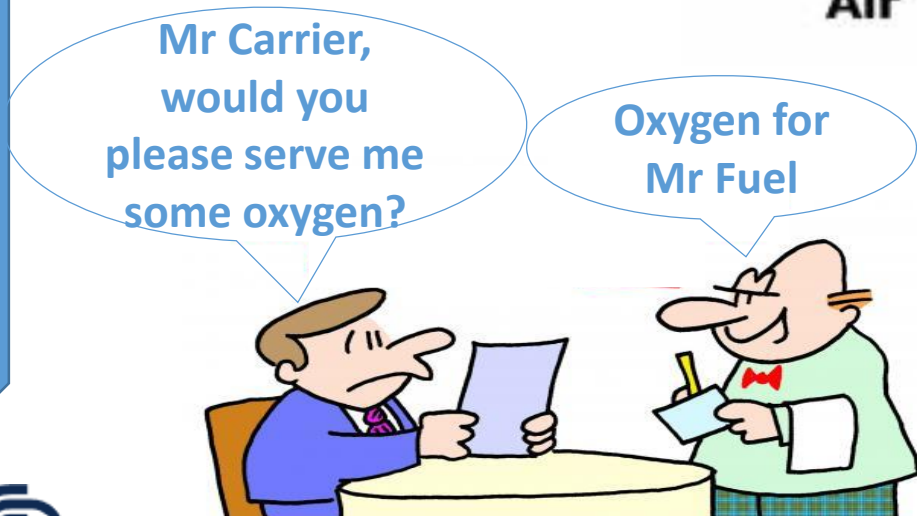
- **Oxidation : exothermic**



- **Reduction : endothermic**

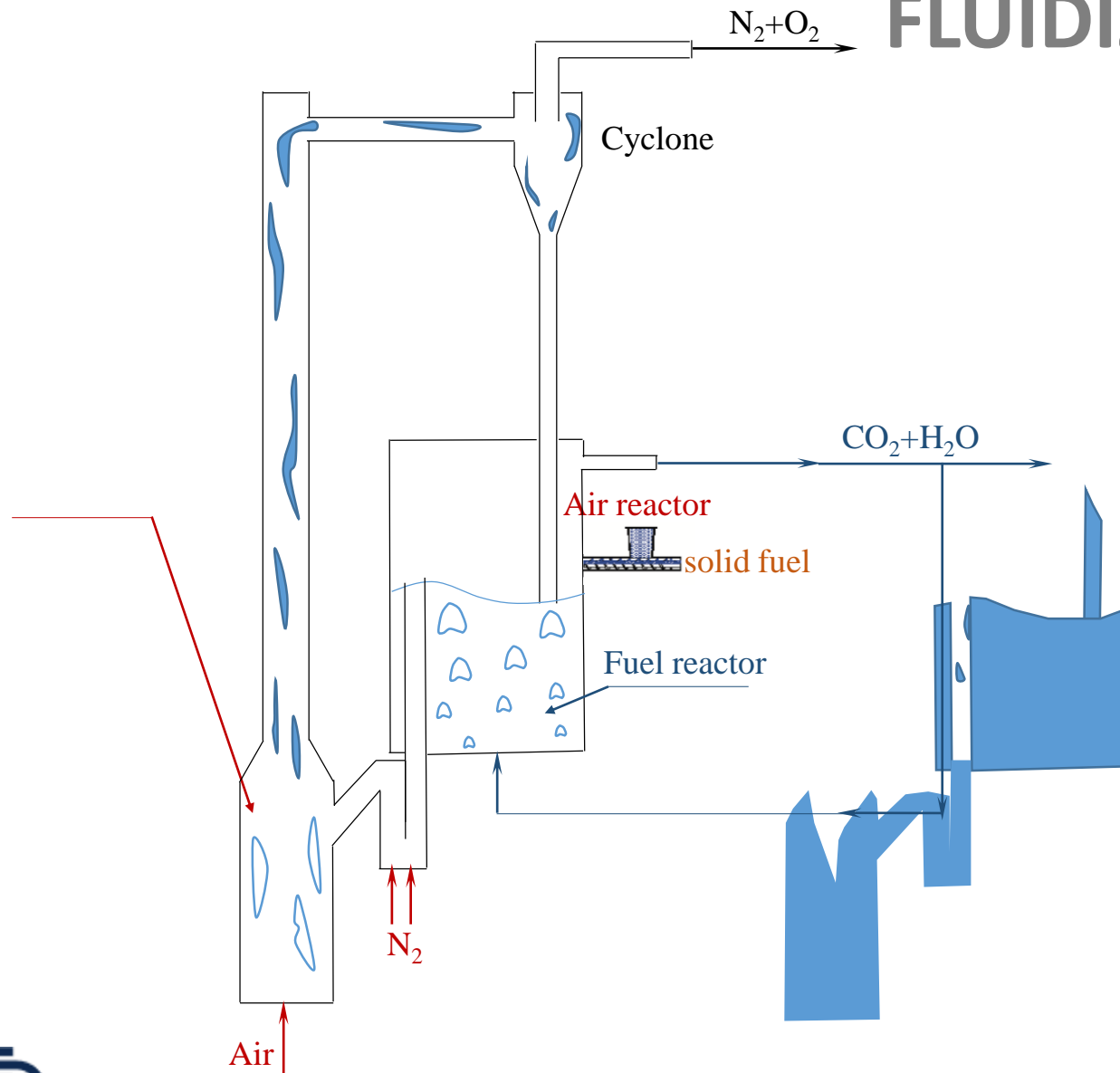


M : metal, MO : metal oxide

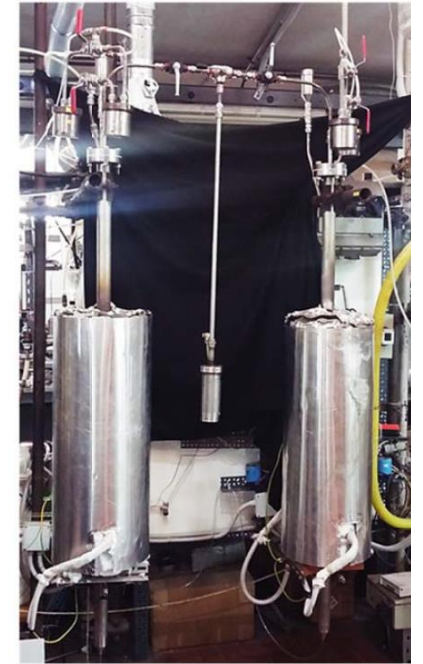
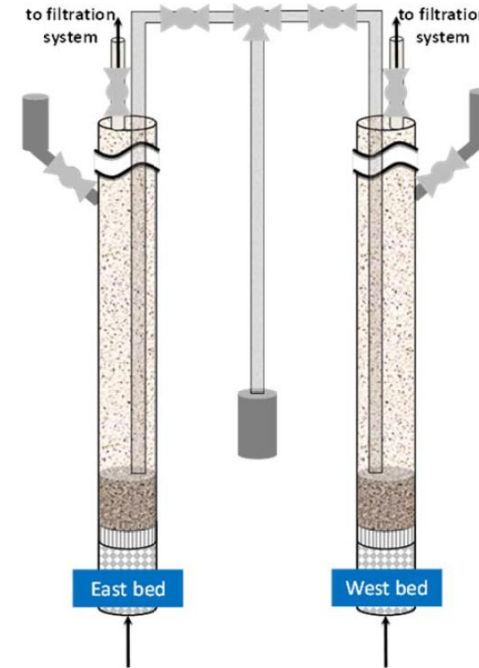


THE "GOOD" WAITER

DUAL INTERCONNECTED FLUIDIZED BEDS FOR CLC



Ping pong reactor
for lab scale testing



Oxygen carriers

- ✓ High reactivity
- ✓ Good selectivity
- ✓ High oxygen storage capability
- ✓ No carbon deposition
- ✓ Environmental friendly
- ✓ No attrition
- ✓ No agglomeration
- ✓ Long lifetime over high temperature redox cycles

In a natural gas-fired CLC system, operating at 10 bar with an oxygen carrier consisting of NiO on alumina (\$15.3 per kg) to break even with a NGCC system fitted with an amine scrubber, the particles would have to last 500-700 hours.



Ni-based oxygen-carriers

- ✓ very high reactivity with almost complete CH_4 conversion
- ✗ prone to carbon deposition .

Cu-based oxygen-carriers

- ✓ high reaction rates and oxygen transfer capacity
- ✗ high tendency to agglomeration

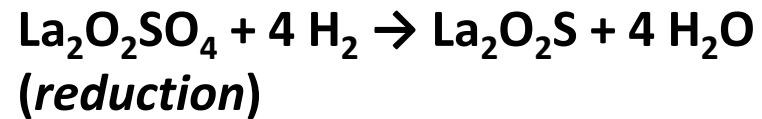
Fe-based oxygen-carriers

- ✓ low cost and environmental compatibility
- ✗ low CH_4 conversion and low oxygen transport capacity

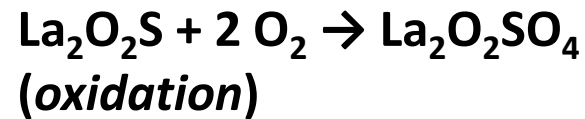
Novel oxygen carriers for Chemical Looping Combustion at STEMS

Lanthanum oxysulphates doped with transition metals (Co, Mn, Cu)

5% CH₄/air cycles @800°C over Co-doped lanthanum oxysulphate



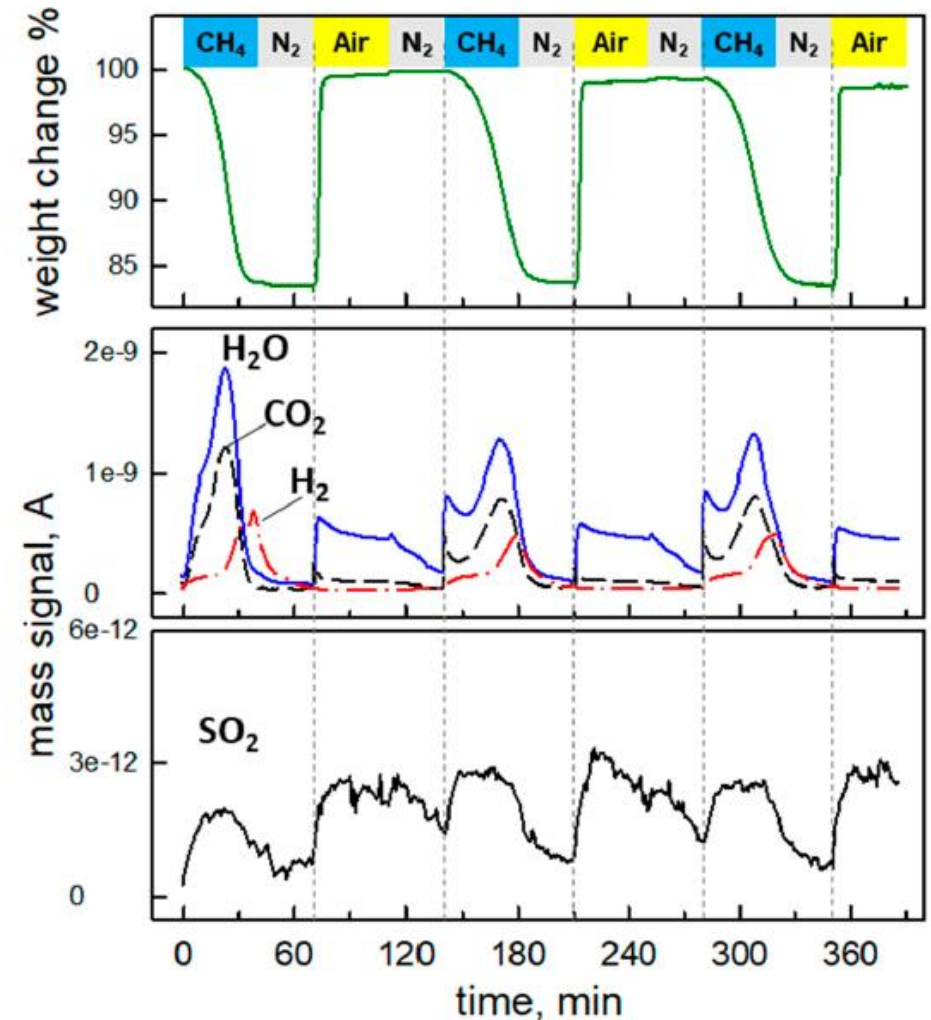
Repeatable cycles
Stoichiometric
reduction/oxidation



High selectivity to H₂O
and CO₂

Doping with transition
metals increases both
performances and thermal
stability of La₂O₂SO₄

Negligible
degradation of carrier
by sulphate
decomposition

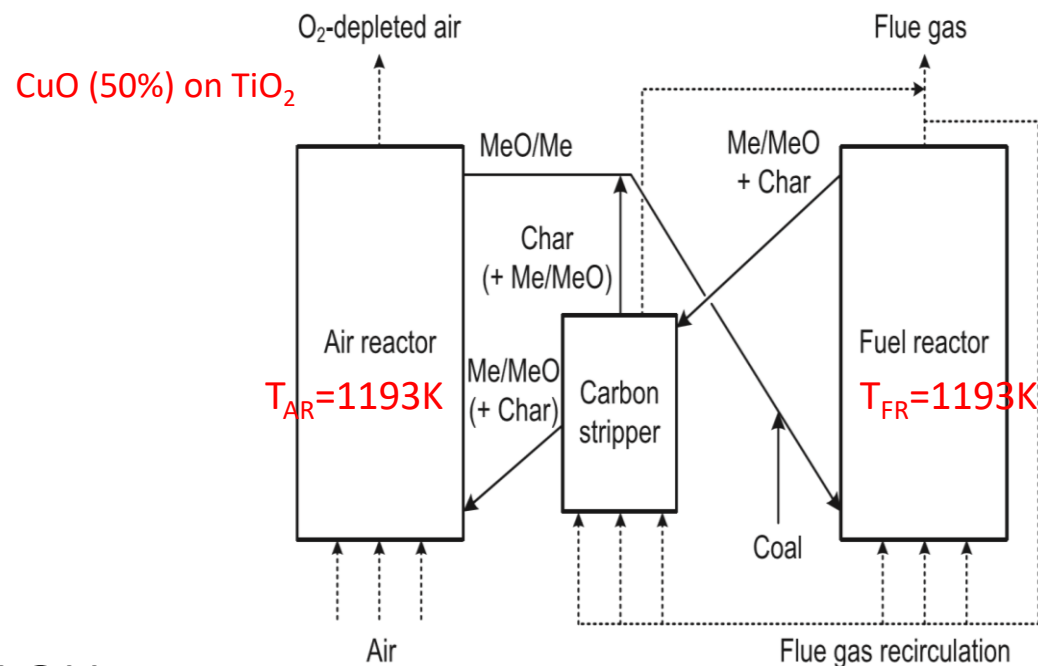


Capture ready combustion

Chemical Looping Combustion (CLC) of solid fuels

Is difficult because we cannot realize the contact between the solid carrier and the solid fuel

1. Coal is firstly gasified and then, CLC for gases is applied
2. Gaseous oxygen is released from the metal carrier to burn coal (Chemical looping with oxygen uncoupling, CLOU)

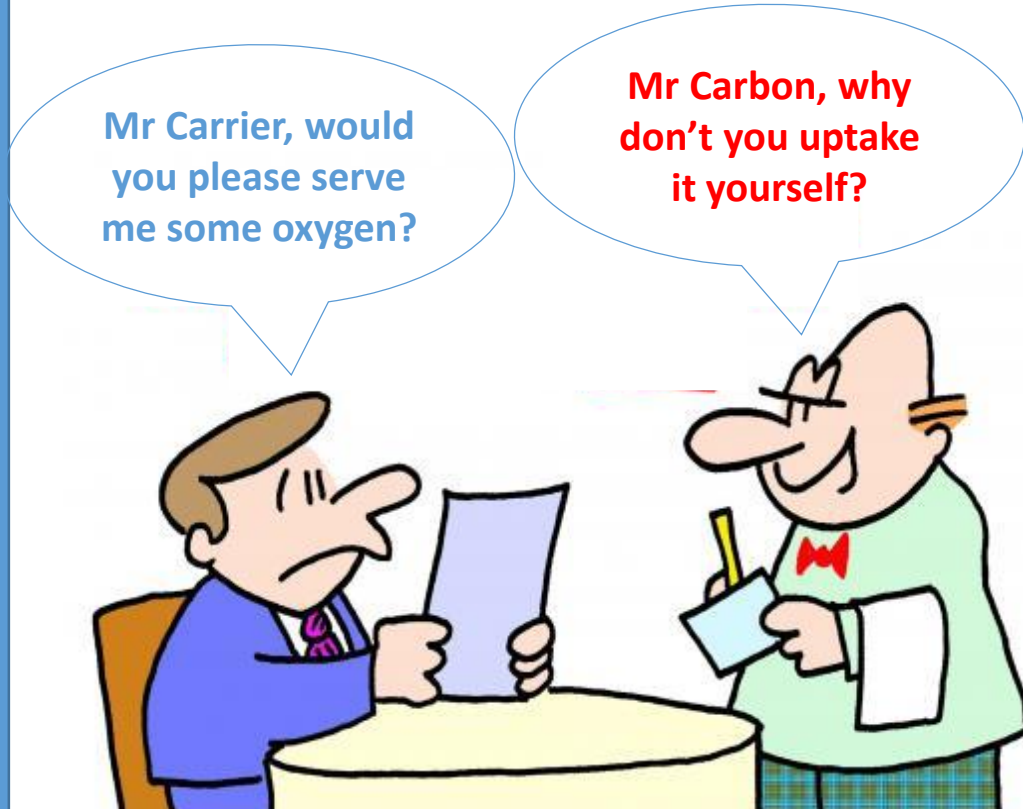


CLOU concept

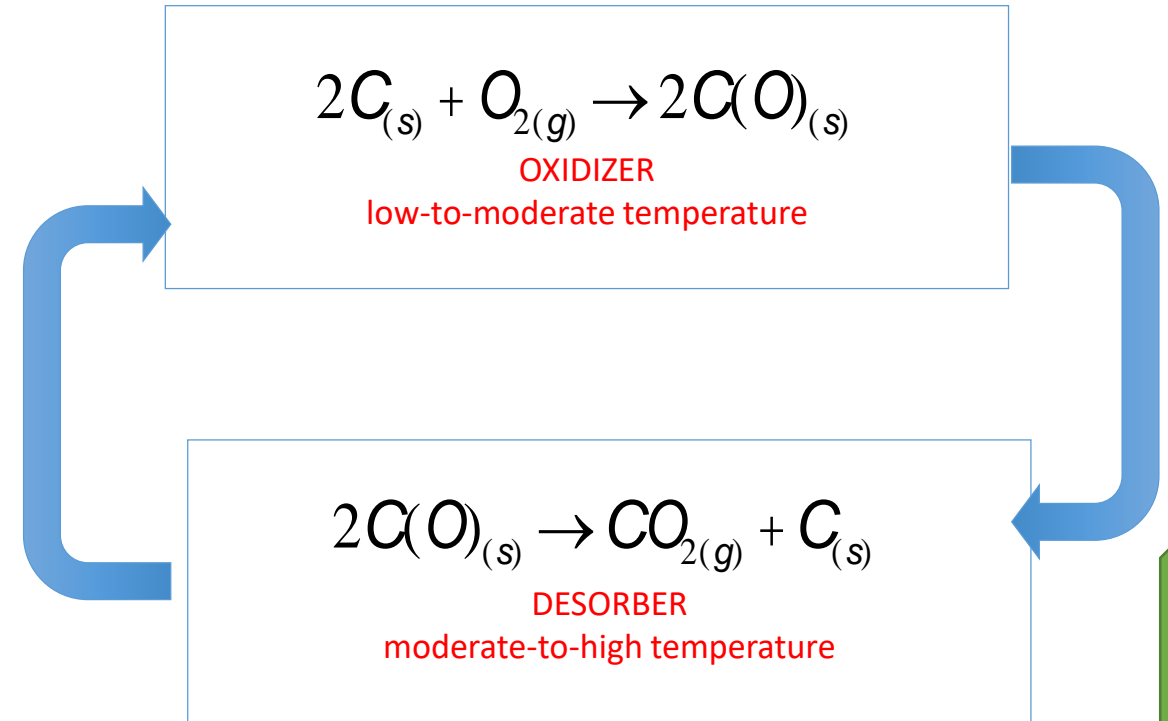


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Capture ready combustion Chemical Looping Combustion (CLC) of solid fuels



THE "LAZY" WAITER



Carboloop concept

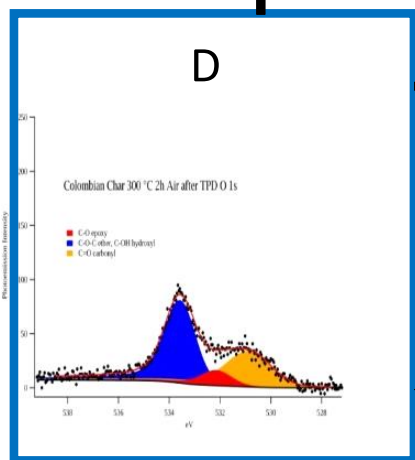
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For materials scientists

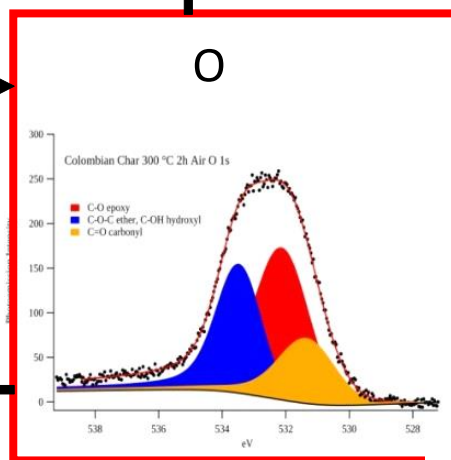
↑ CO₂ +
↑ impurities

↑ Oxygen depleted
air

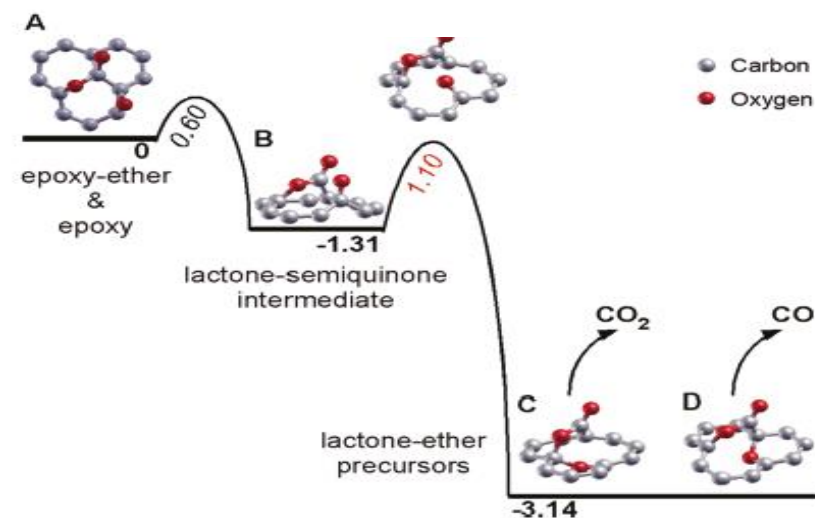
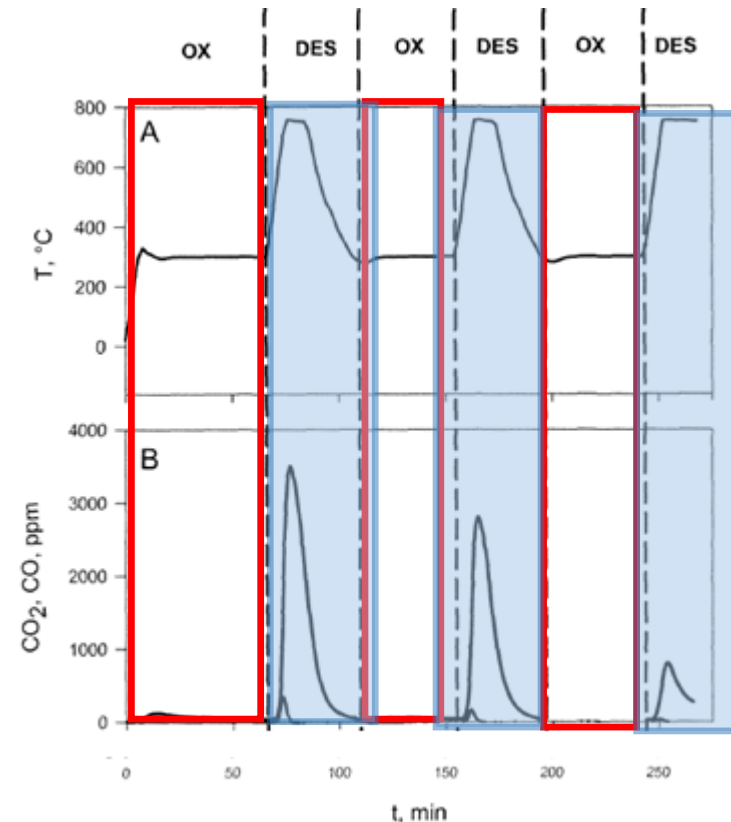


C

C(O)

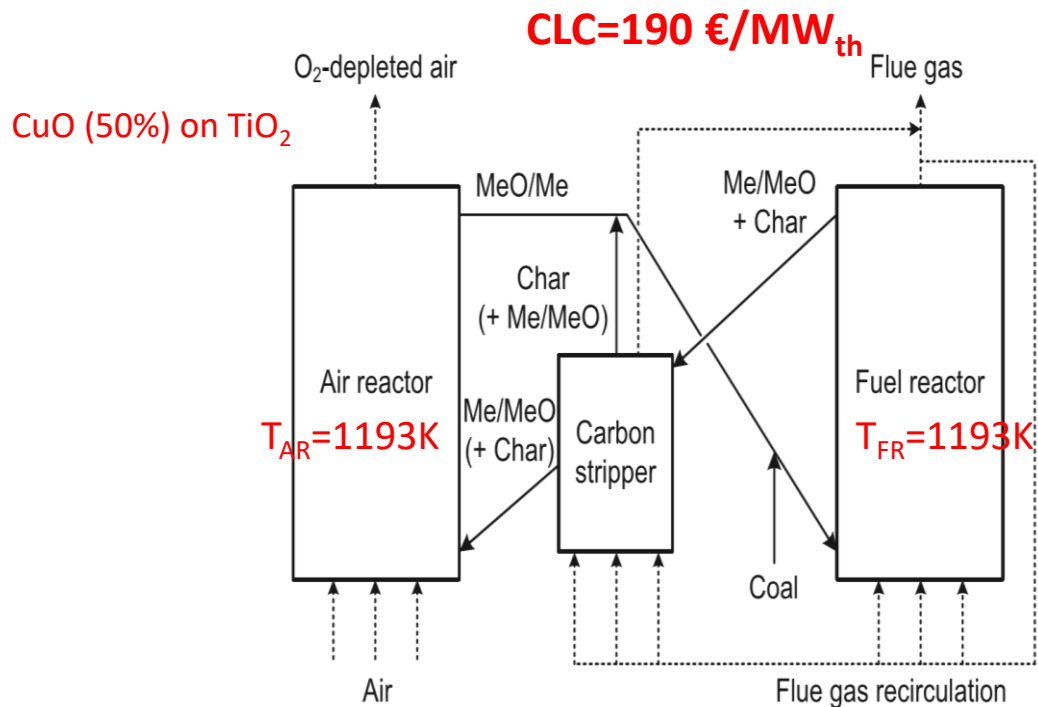


↑ Air

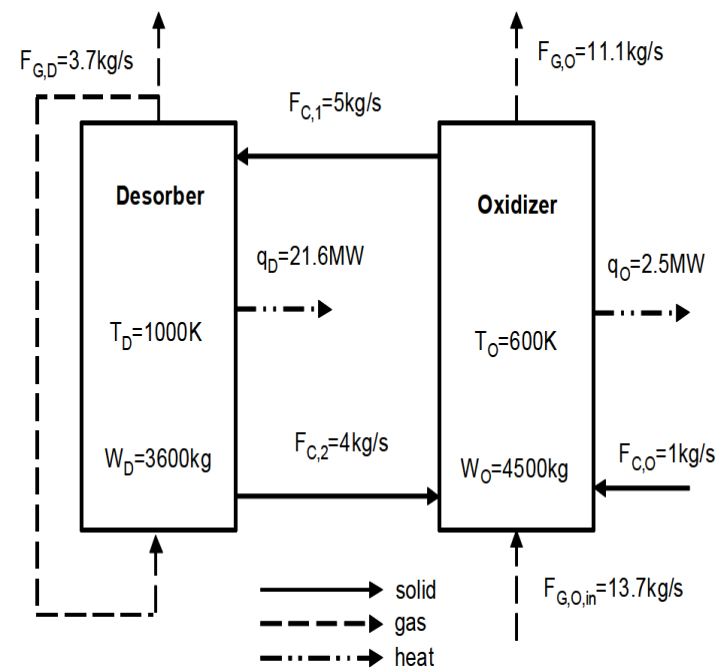


CarboLoop versus metal based CLC for solids

- Less complex (no stripper needed)
- Lower temperature (600-1000K vs 1193s)
- 40 % Lower capital investment cost**



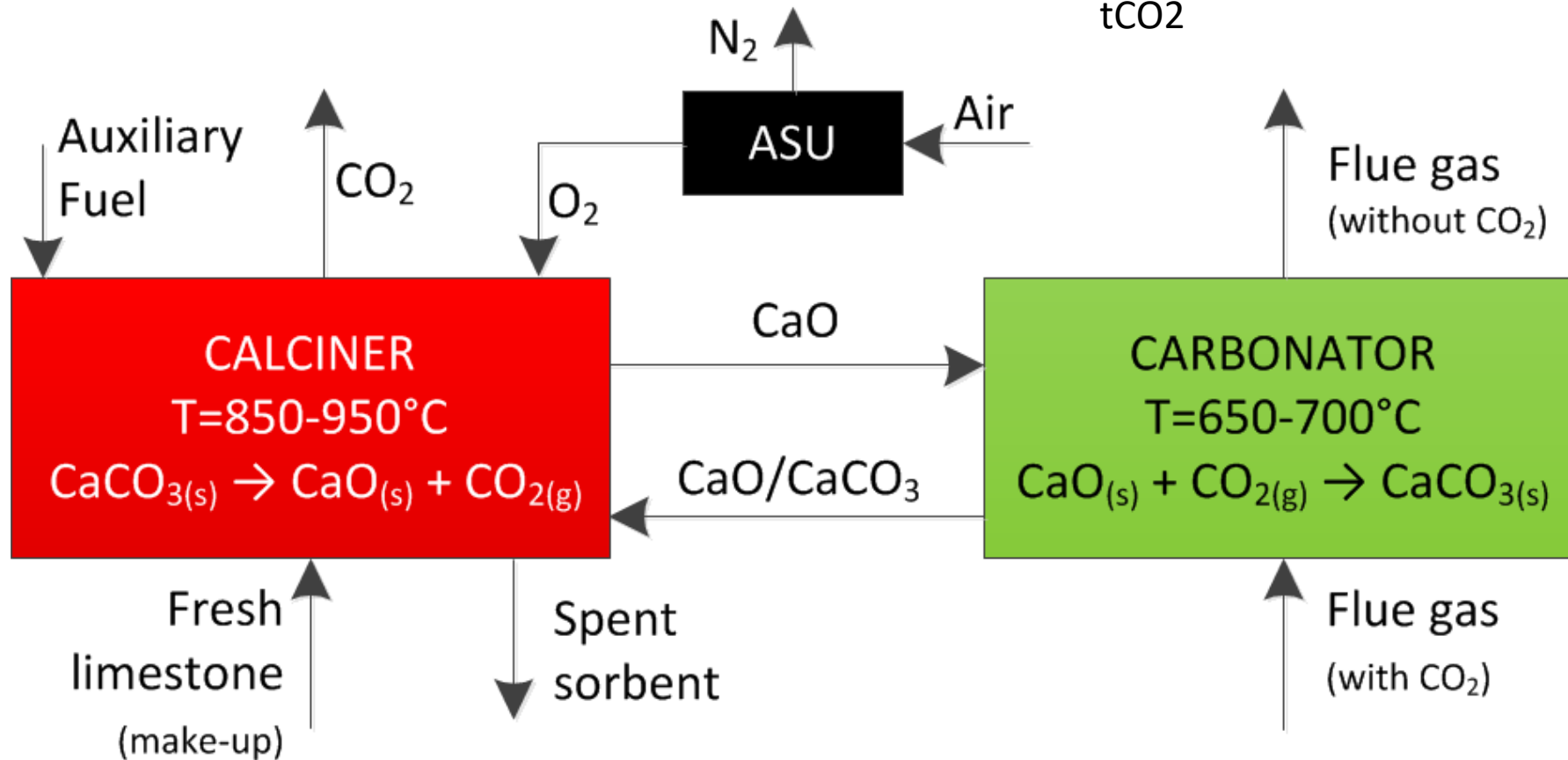
CarboLoop= 107 €/MW_{th}



From M. Spinelli et al. / Energy 103 (2016) 646e659

CO₂ capture: Calcium Looping

- TRL 6-7
- Calcium looping can be combined with cement industry
- Costs are in the order of \$30 per tCO₂ (like MEA)
- Integrated CaL process would offer a carbon capture cost of less than \$30 per tCO₂



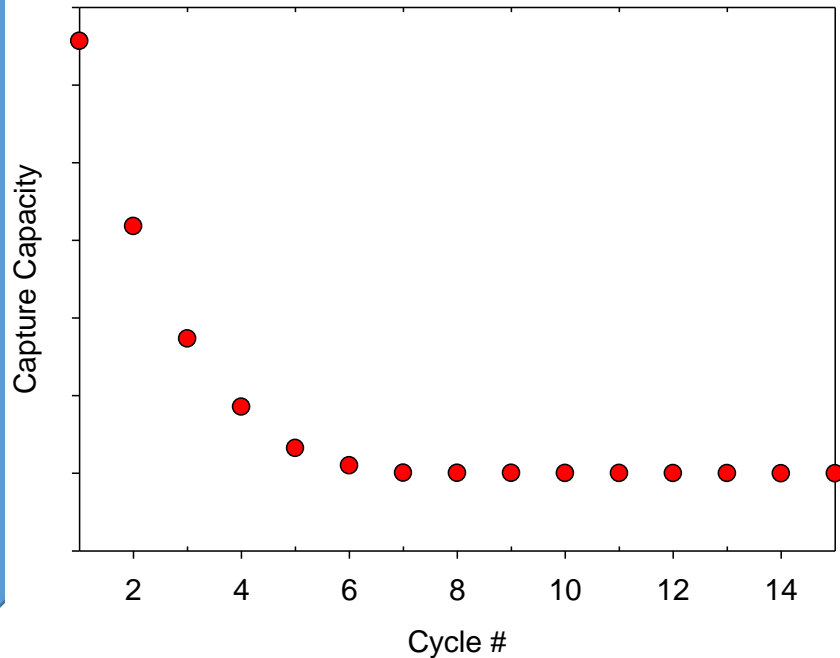
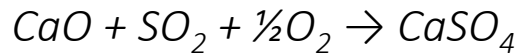
Ca-L for materials scientists

Decay of CO₂ Capture Capacity of the sorbent



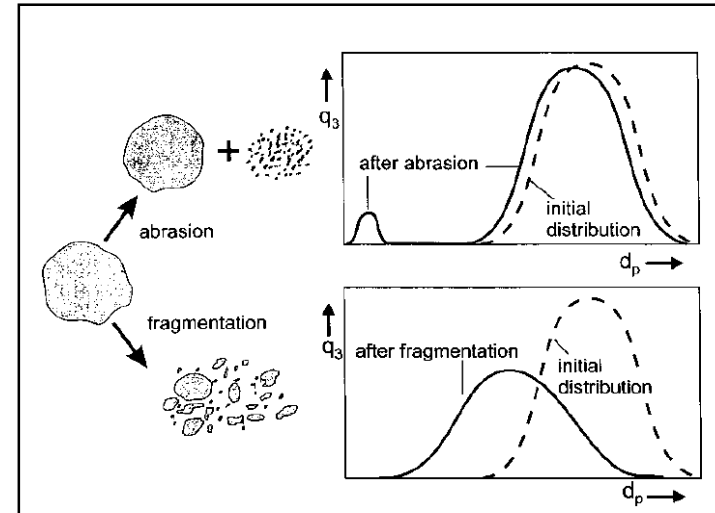
➤ Sintering

➤ Presence of SO₂



Attrition/Fragmentation Phenomena

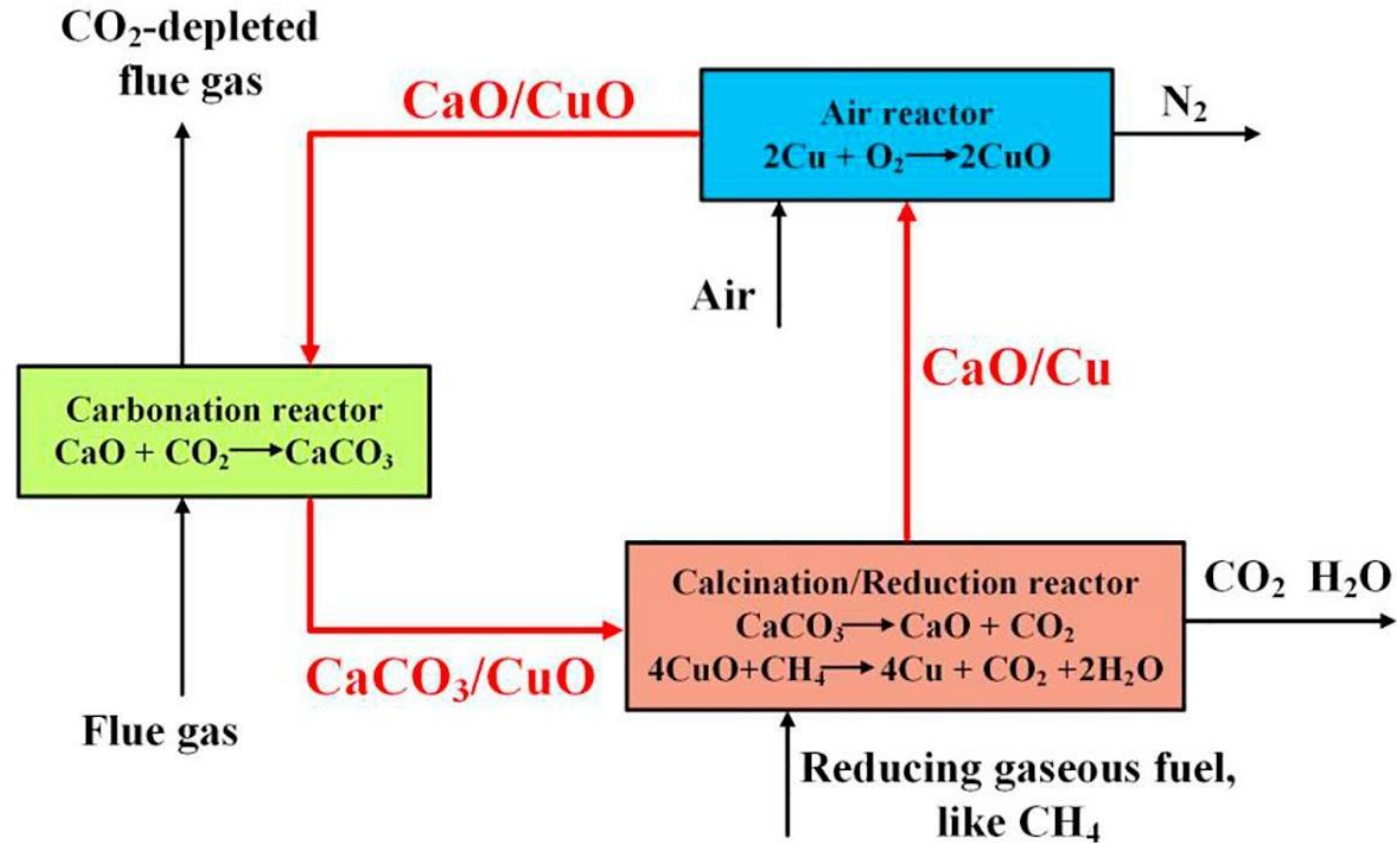
- Primary Fragmentation
- Secondary Fragmentation
- Attrition by Abrasion



Modified sorbents:

- hydration, re-carbonation, doping with various reagents, pelletization, thermal pre-treatment, sol-gel or precipitation of calcium carbonate, preparation of nano-materials
- Some additives may actually weaken the resulting sorbent which fragment under FB conditions

CO₂ capture: Calcium Looping +CLC

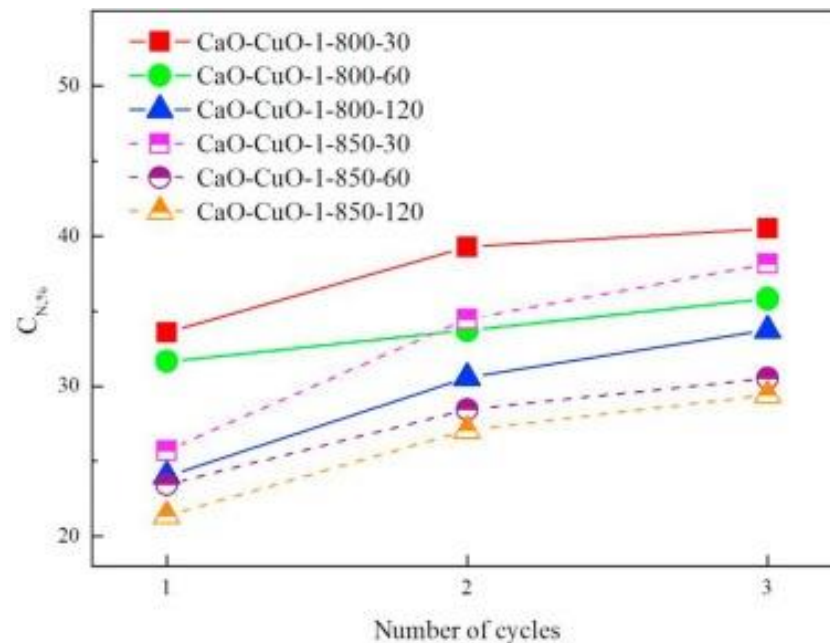
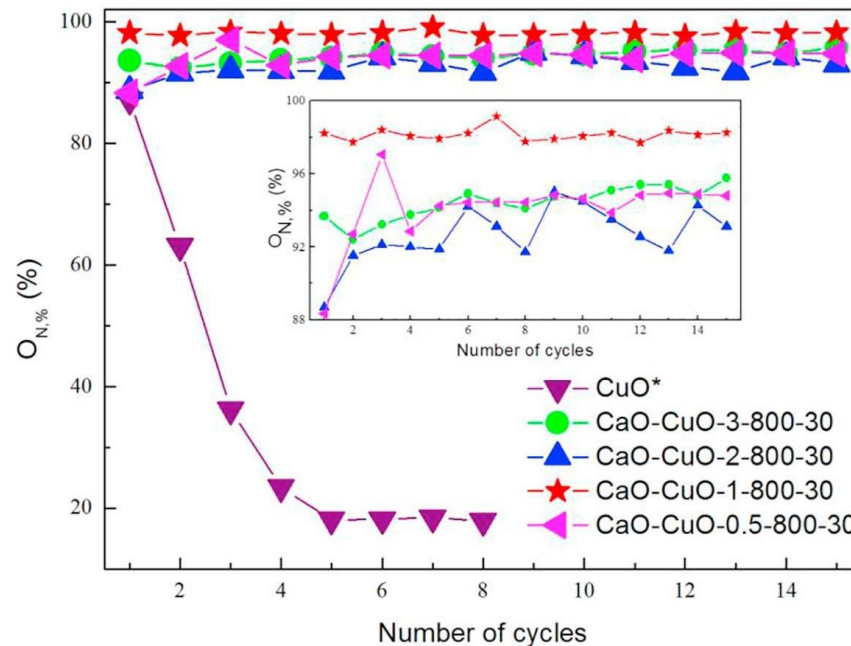
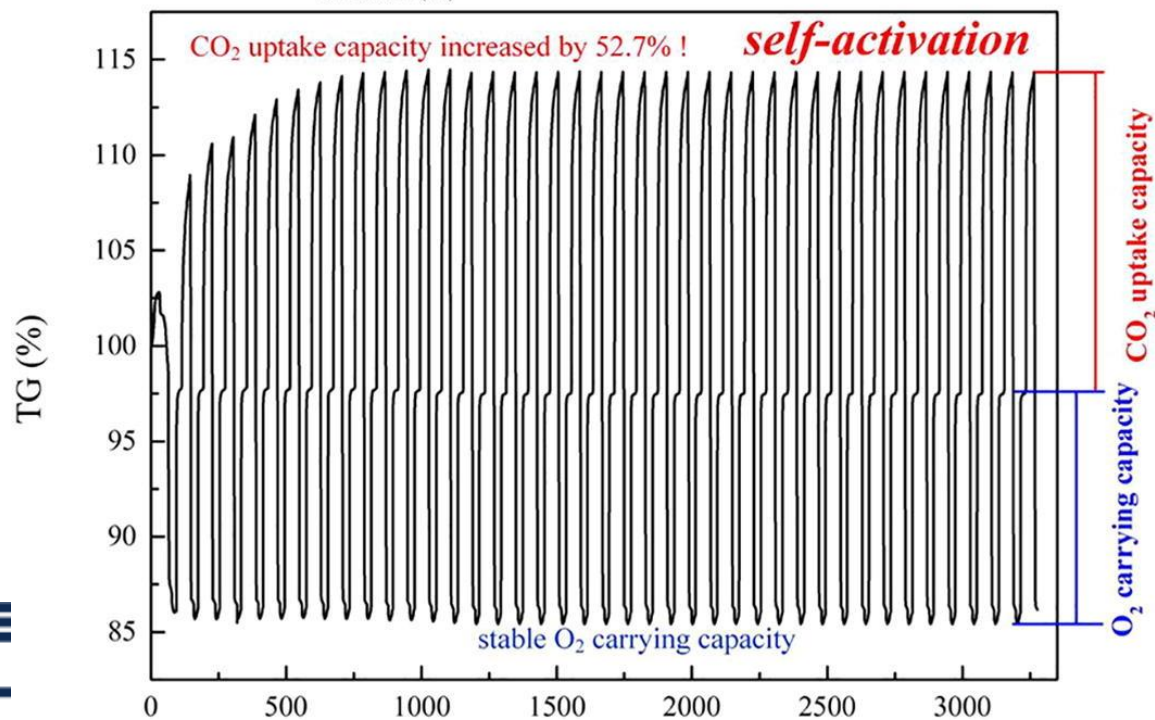
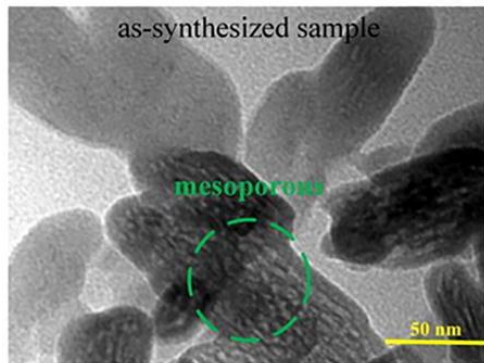
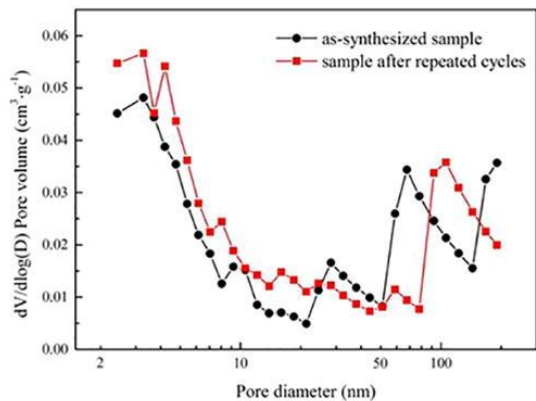


Self-activated, nanostructured composite for improved CaL-CLC technology, Edward J. Anthony, Chem Eng. Journal 2018



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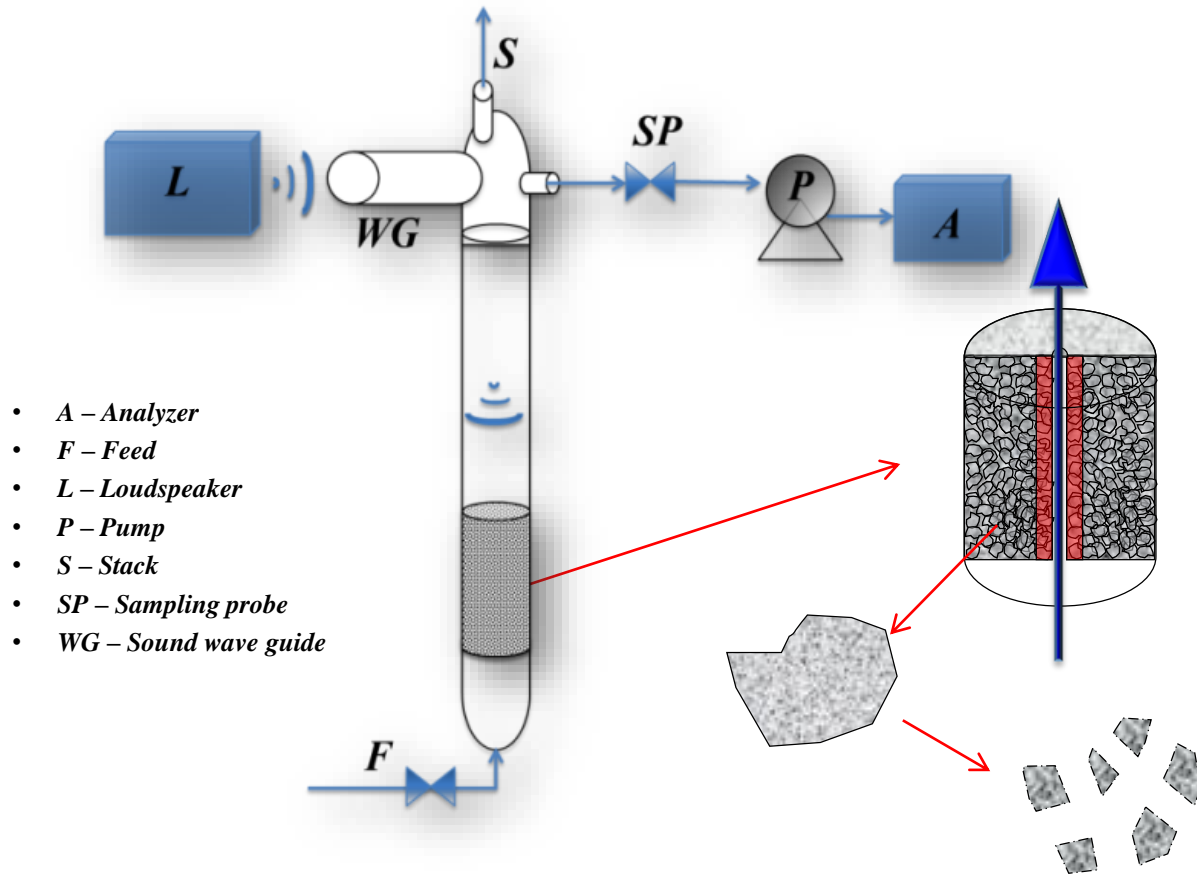
Materials in CaL+CLC



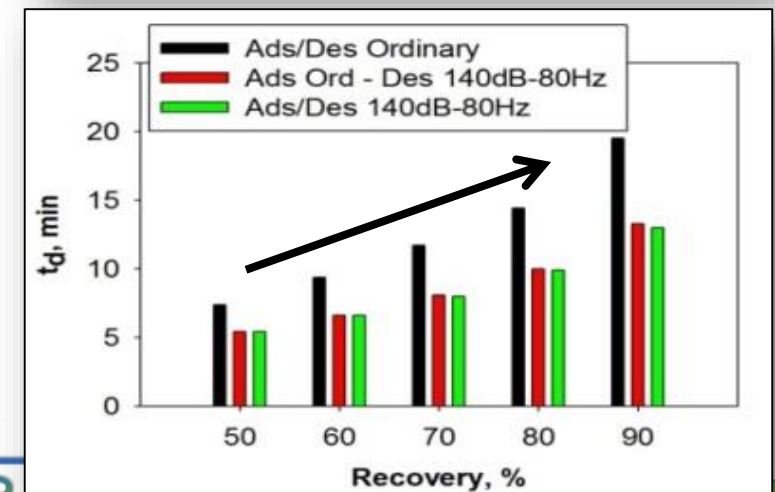
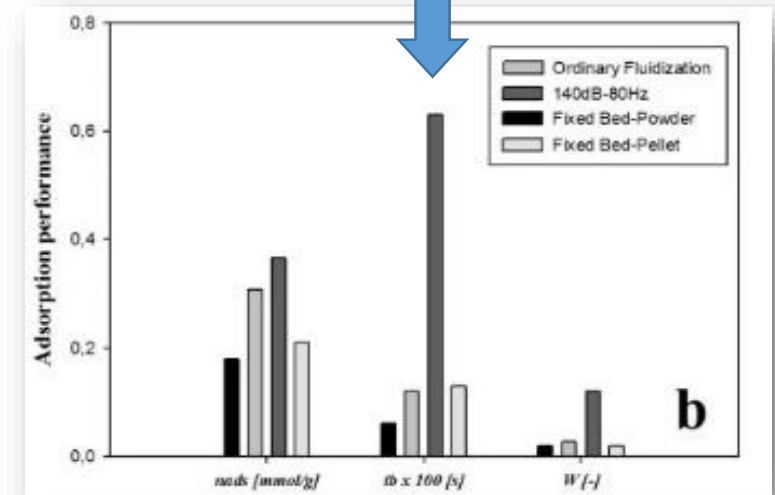
CO₂ capture: fine powders in a sound assisted fluidized bed

- 1.78 MJ/kgCO₂ (against 3.6-4 in case of MEA)
- Tested with low percent of CO₂

Effect of sound



- *A* – Analyzer
- *F* – Feed
- *L* – Loudspeaker
- *P* – Pump
- *S* – Stack
- *SP* – Sampling probe
- *WG* – Sound wave guide



Link between adsorption performances and porosity

Adsorption performances

HKUST-1

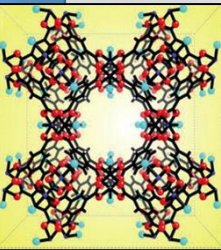
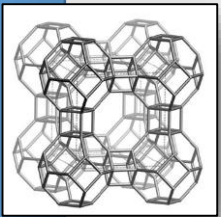
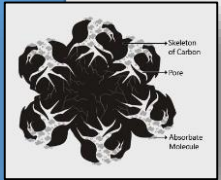
CB-FM

AC Sigma

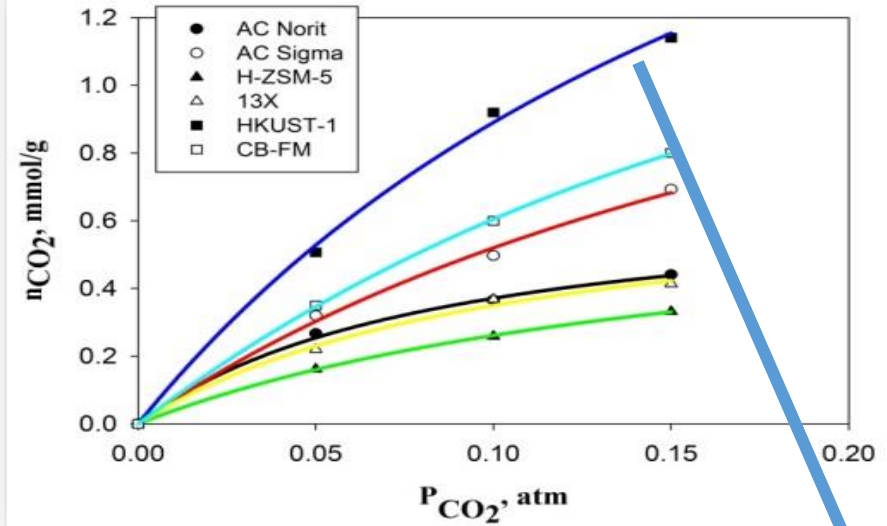
AC Norit

13X

H-ZSM-5

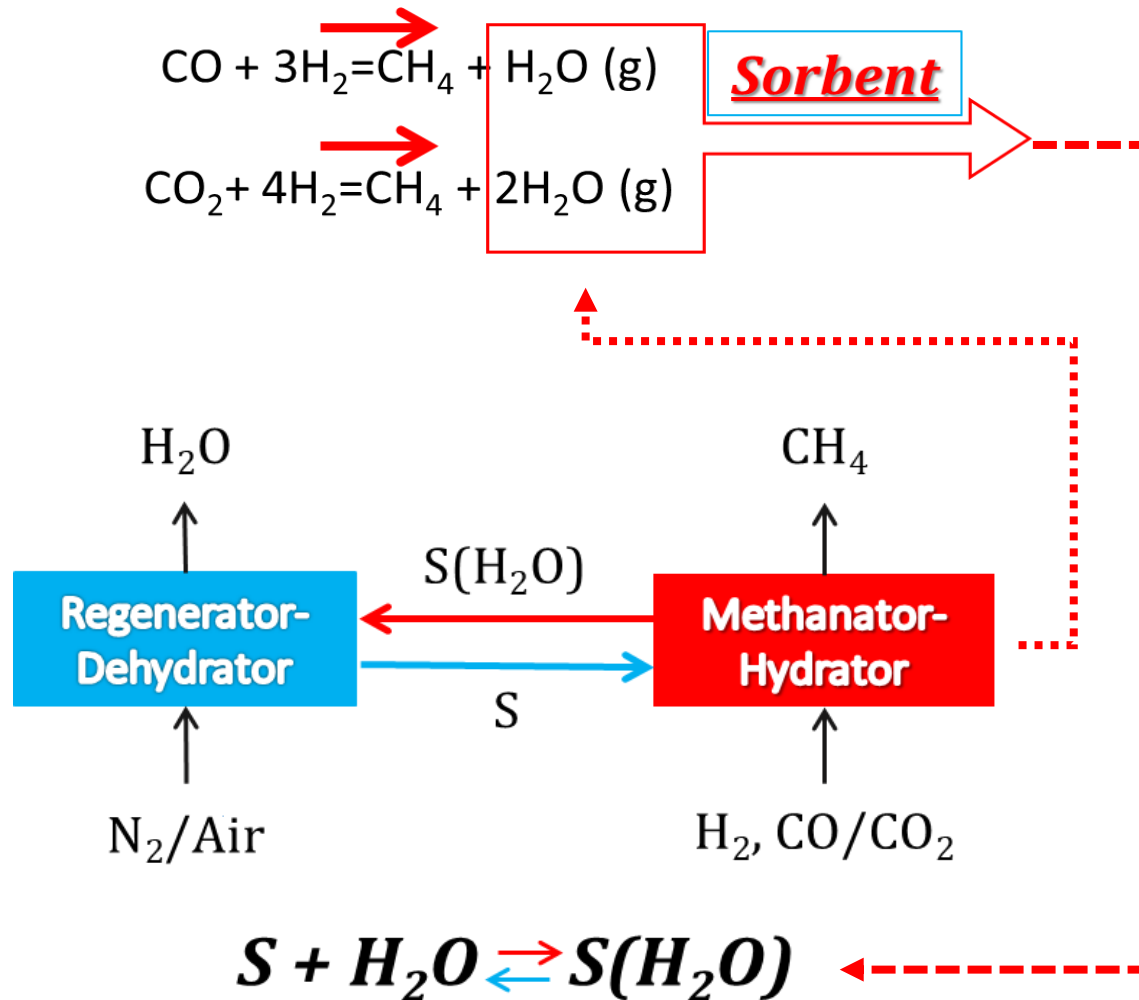


↑
Wednesday
at 10.00,
Michela Alfé



Materials	BET, m ² /g	Pore volume, cm ³ /g
AC Norit	1060	1.34
AC Sigma	1038	1.14
H-ZSM5	400	0.41
13X	960	0.41
H-KUST-1	680	0.66
CB-FM	157	1.05

CCU: Chemical Looping Sorption Enhanced Methanation (CL-SEM)



Methanation: $T > 300^\circ\text{C}$

Regeneration: $T > 400^\circ\text{C}$

Advantage: lower pressures compared to commercial methanation (fixed bed-adiabatic stages).

-Need for tailored sorbents

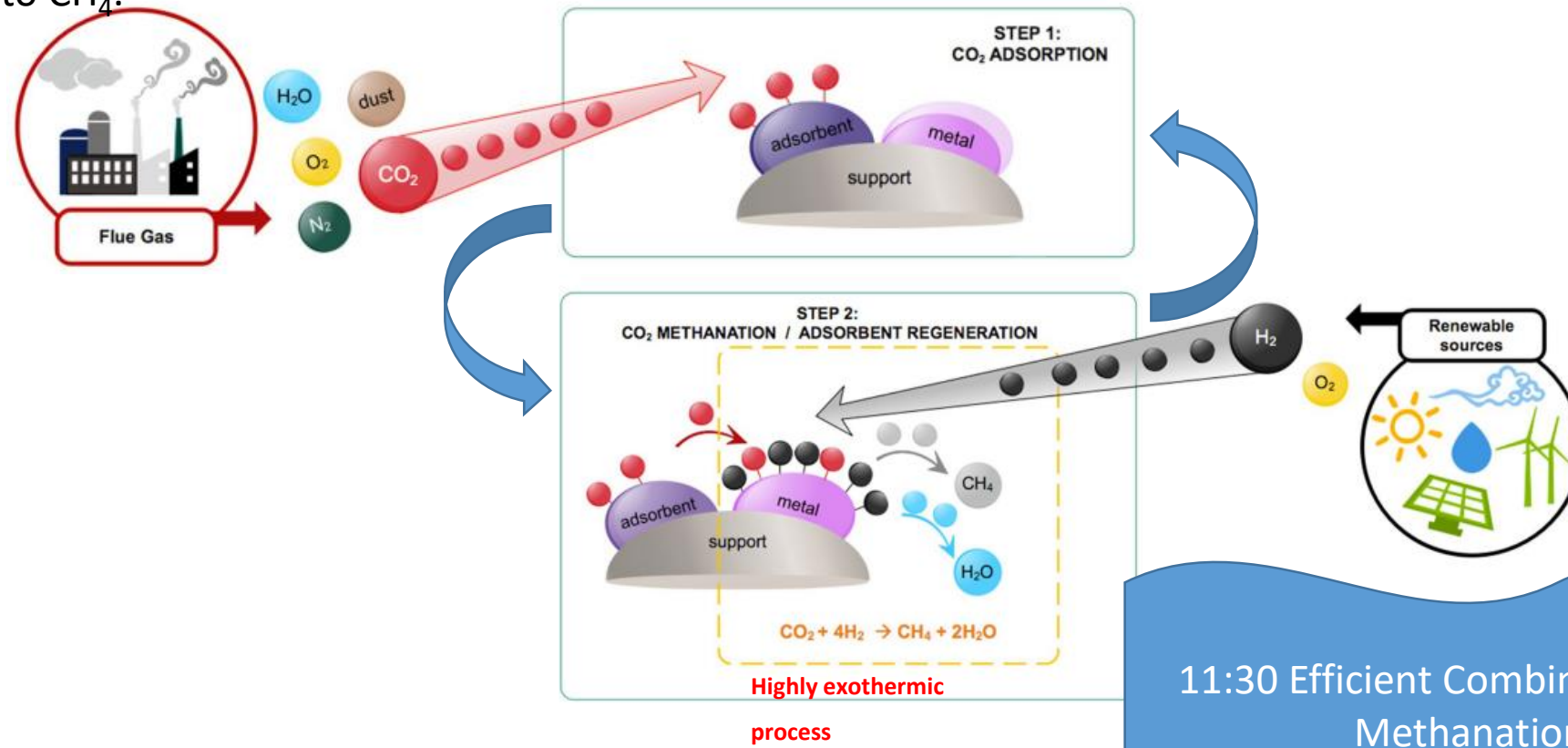
So far CaO and a 3A zeolite have been tested

-3A zeolites (low adsorption capacity) CaO fragile and active towards CO_2

CCU: Combined CO₂ Capture & Methanation

Dual Function Materials capture CO₂ from industrial flue gases (or even air) and release it as concentrated synthetic natural gas (SNG)

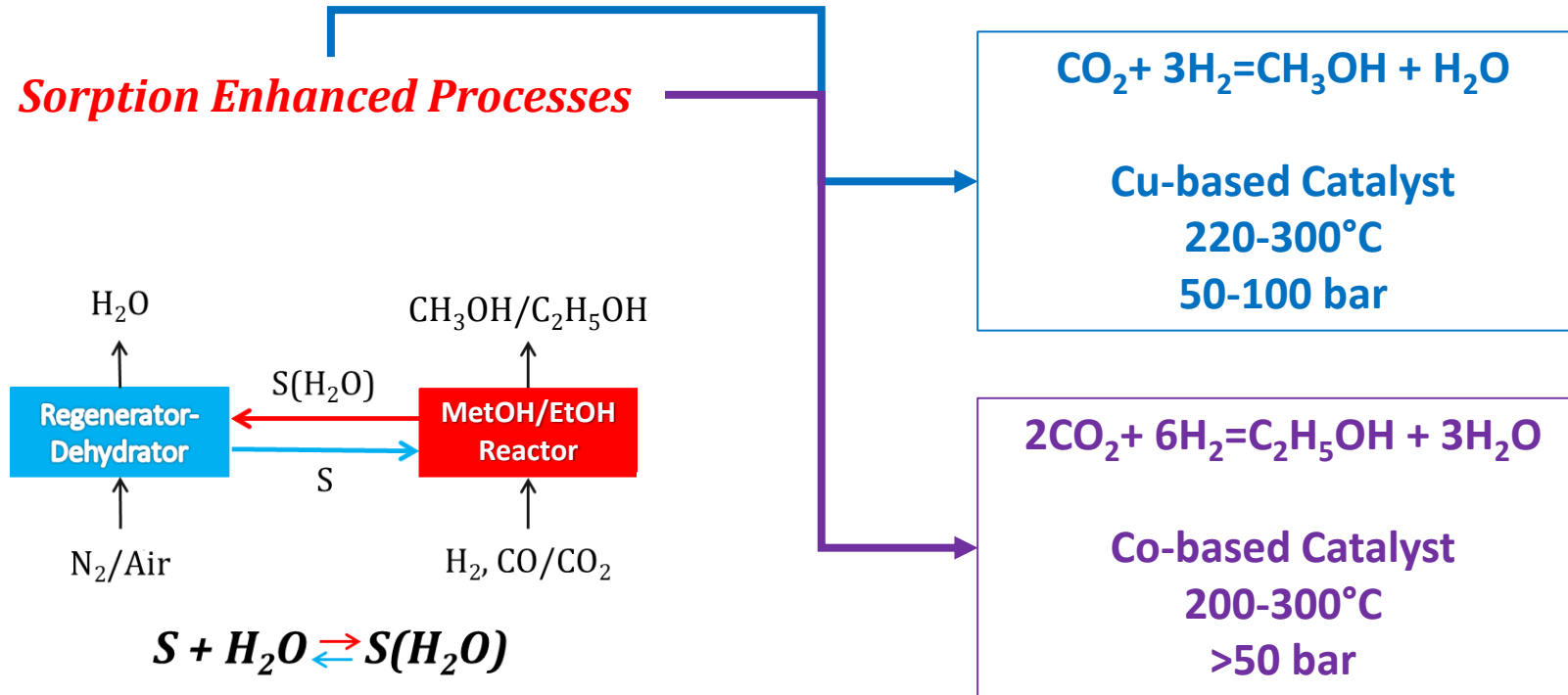
Two key capabilities: 1) large & fast CO₂ adsorption 2) high catalytic activity for the hydrogenation of CO₂ with high selectivity to CH₄.



11:30 Efficient Combined CO₂ Capture and Methanation S. Cimino

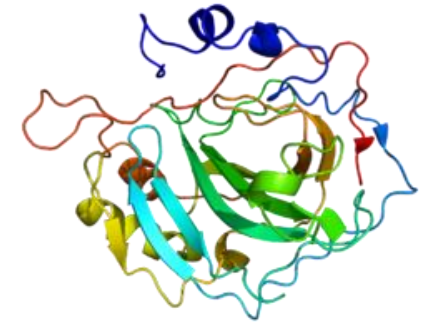
CCU: CO₂ Capture & Met-OH production

PtL-MetOH/EtOH



CCU: enzymatic CO₂ capture and utilization

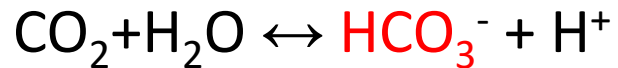
human Carbonic anhydrase II



Who? **Carbonic anhydrase (CA)** (EC number 4.2.1.1):

enzyme expressed in different forms in most of the living organisms and microorganisms

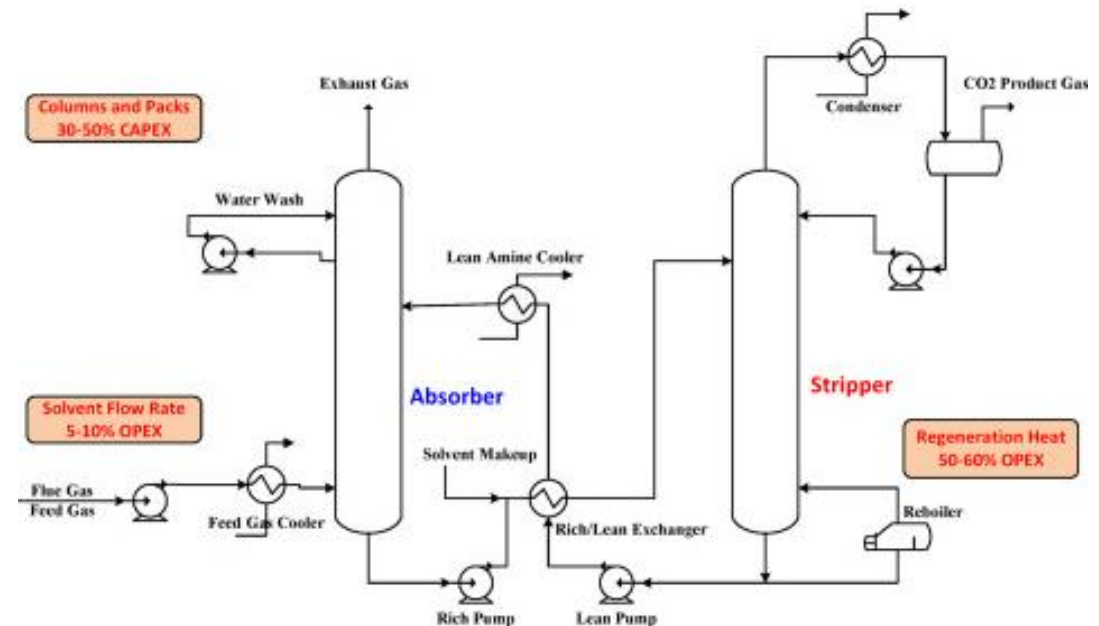
What? Catalyzes **CO₂ hydration reaction**



Reactive CO₂ absorption in aq solvents (KCO₃, NaCO₃, ...)

Where? Post combustion in power plants, industrial plants

Why? **Alternative to amines as absorption rate promoter:** advantages in use of CA in case of CO₂ conversion in aq phase → construction materials through mineralization, microalgae cultivation, biochemical CO₂ fixation (enzyme cascade)



Materials enzymatic CO₂ capture and utilization

Enzyme immobilization: enabling the use of CA in continuous CO₂ absorption units (e.g. packed columns, bubble columns, G-L membrane, ...)

CA immobilization:

Confines CA into CO₂ capture units: **biocatalyst morphology** ↔ reactor design

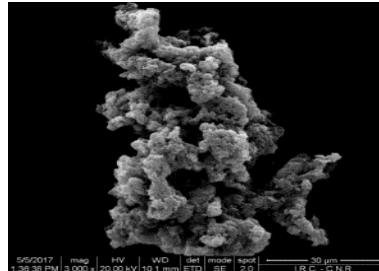
Stabilizes CA up to 70-80°C

CA covalent attachment on solid supports

- Paramagnetic nanoparticles
- Polymeric resins
- Siliceous supports
- Tube wall (membrane)
- Monolith

CA Cross Linked Enzyme Aggregates (CLEA)

Carrier free biocatalyst

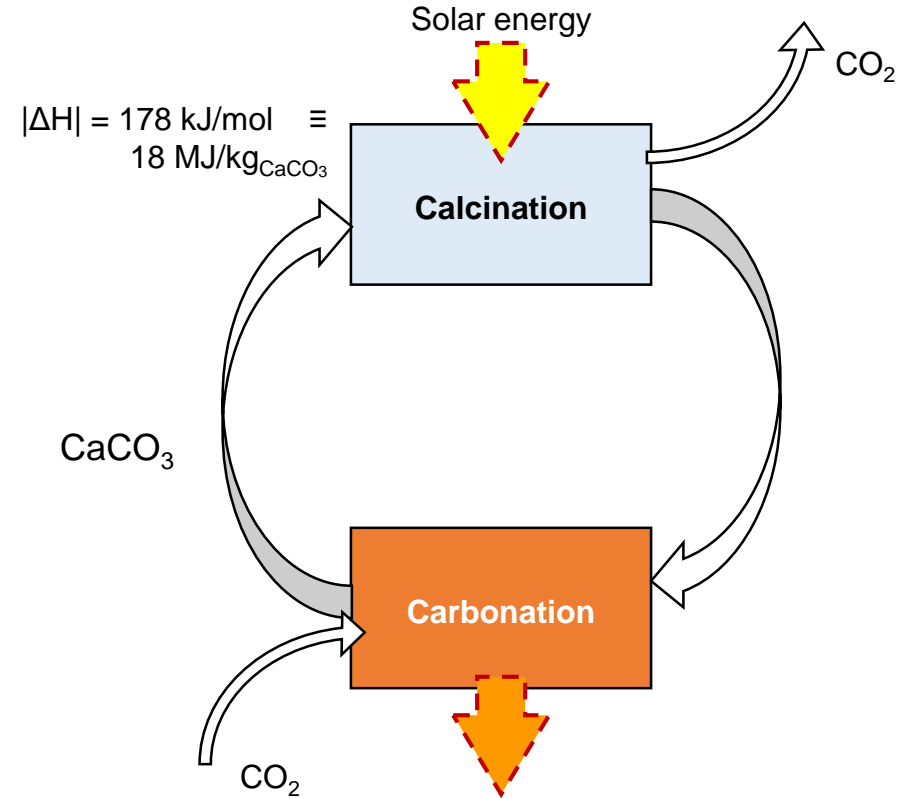
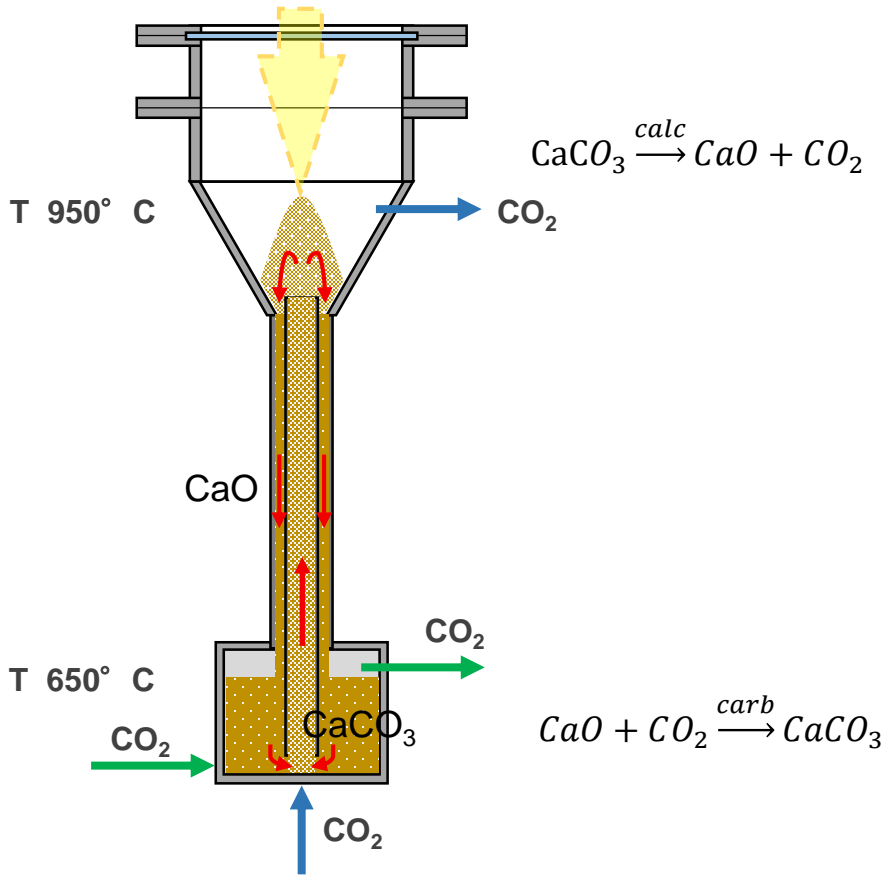


In vivo immobilization

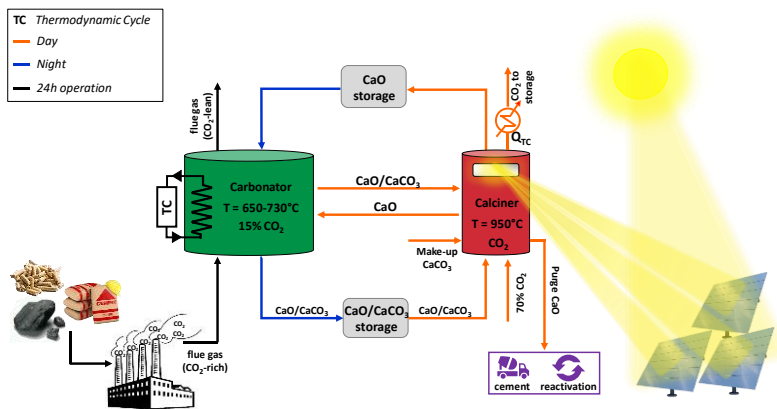
CA as cell membrane protein:
biocatalyst → cell membrane debris dispersed in liquid solvent

CCU and solar energy: CaL with solar energy

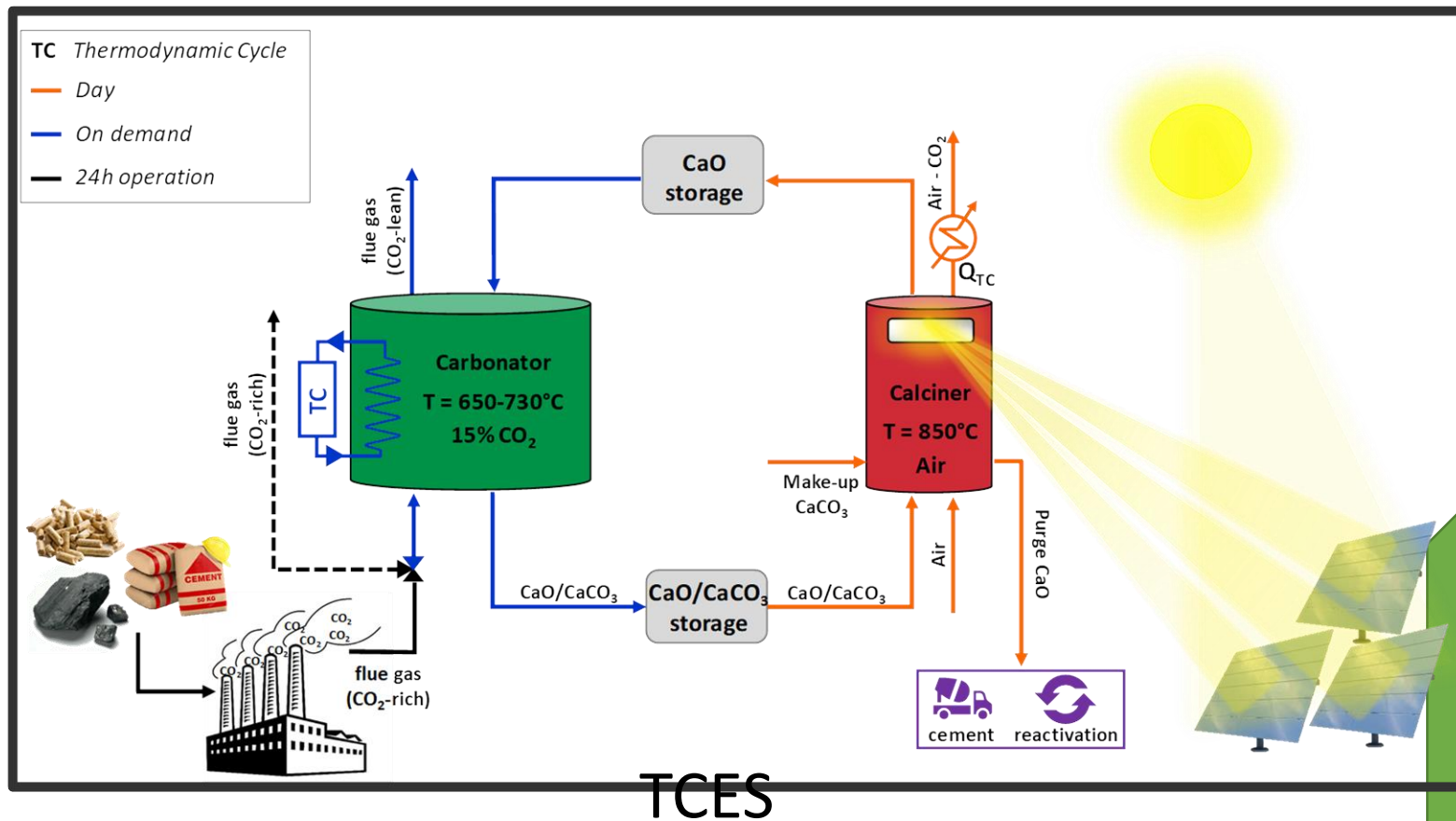
Concentrated solar radiation



SOLAR CALCIUM LOOPING: Thermochemical energy storage (TECS)

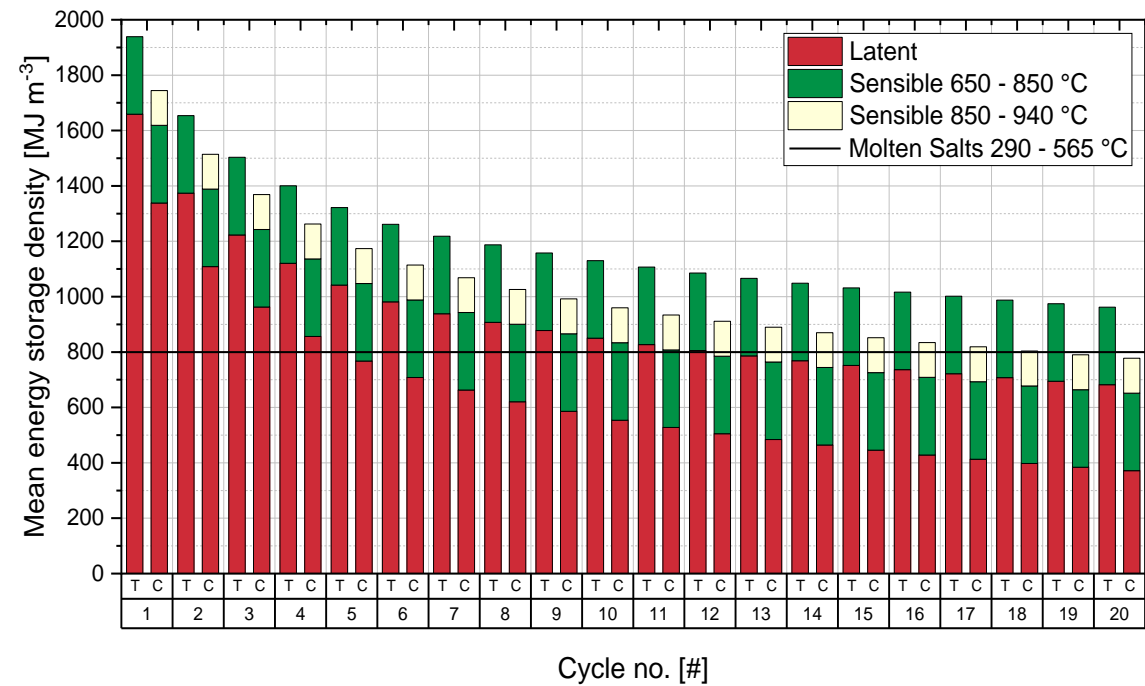
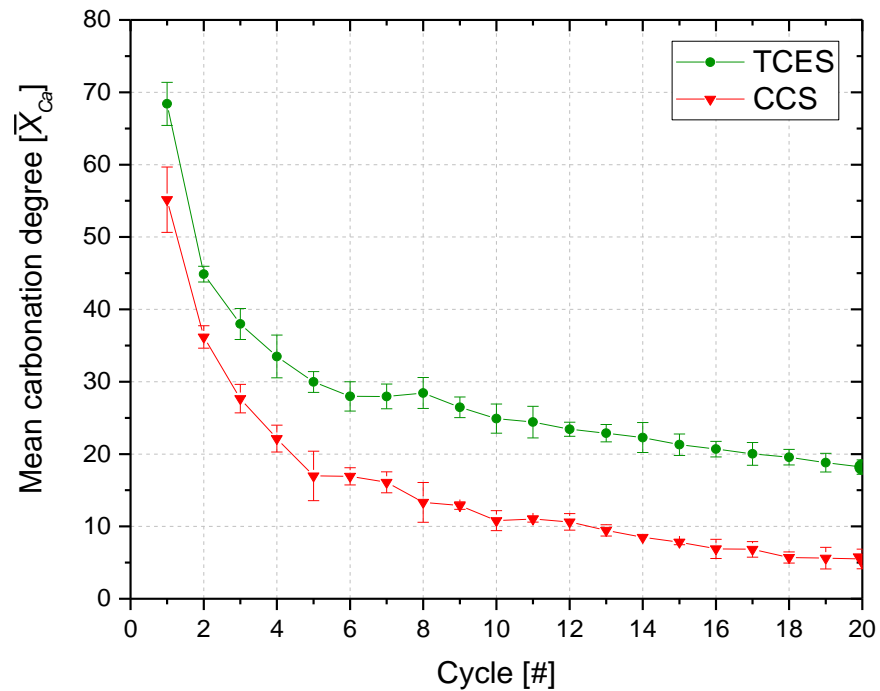


CCS



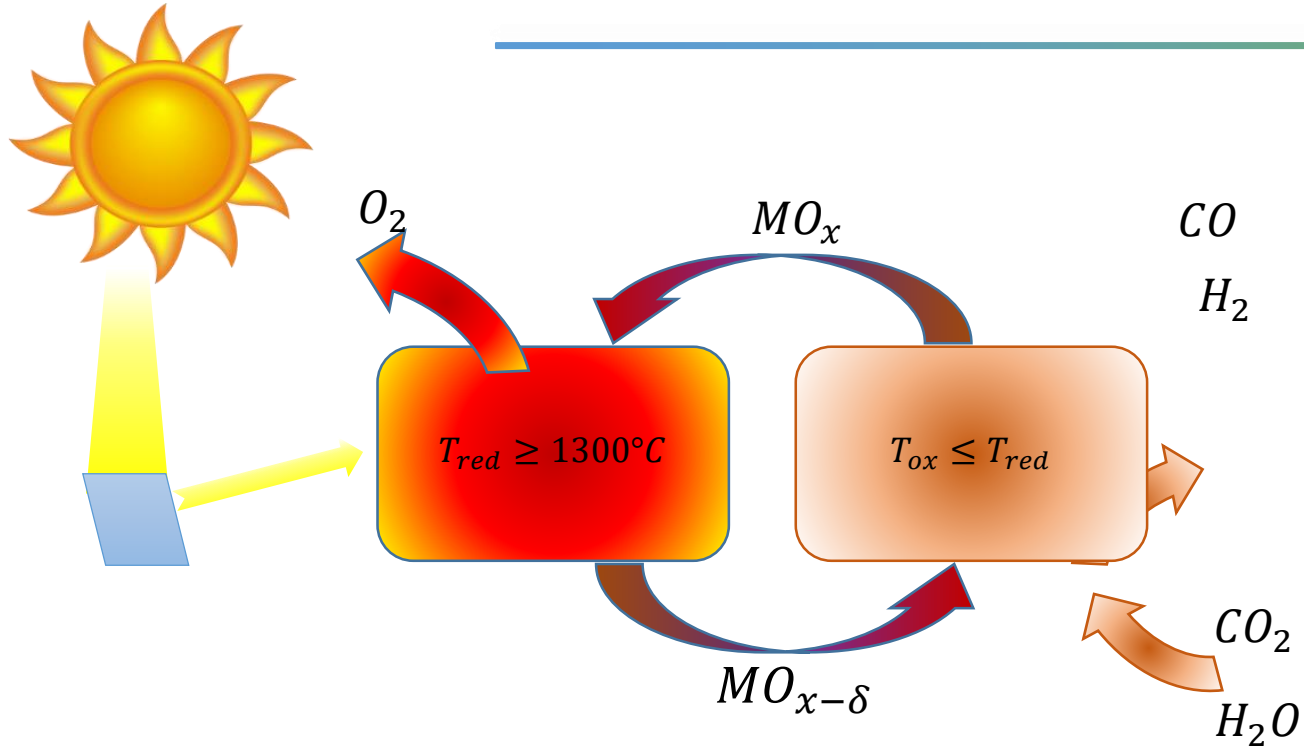
TCES

Solar calcium looping: CCS vs TCES



Tregambi et al., I&ECR (2019)

Solar Thermochemical Splitting



11:45 Thermochemical cycles for CO₂ capture/utilization, R. Solimene/ G. Landi



Cycle	Red. T, °C	Ox. T, °C
Iron oxide	2000-2300	400
Zinc oxide	1600-1800	400
Cerium oxide	1300-1600	1000-1300
Perovskite	1200-1600	800-1000

- Very high temperature (>1300°C)
- Stability of materials

Conclusions

- I tried to provide a very quick overview of research topics in the field of CCSU. I picked some «research topics» that we are currently investigating at STEMS-CNR, but there is much more going on worldwide.
- There is a lot to do for materials scientists in all the fields: CaL, CLC, Capture with solid sorbents, Splitting of CO₂/H₂O, methanation...
- The rate at which new materials progress from the lab- or bench-scale to the pilot-scale is too slow.
- Laboratory-scale work should investigate materials under conditions representative of the real world.
- The take home message is: «process engineers and materials scientists need to work together». Any collaboration is welcome



**Sound assisted capture
in Fluidized beds**

Riccardo Chirone,
Paola Ammendola,
Federica Raganati



Materials for CO2 capture

Michela Alfè



Biotech processes

Maria Elena Russo



Materials for CLC, methanation

Luciana Lisi
Stefano Cimino
G.L. Landi



Loops, CaL, CLC

Antonio Coppola
Massimo Urciuolo
Fabio Montagnaro
(UNINA)
Piero Salatino (UNINA)



Oxyflame

Reinhold Kneer
(RWTH)



CO2 and H2O splitting

Gianluca Landi (Materials)
Roberto Solimene
(reactors)



Solar aided processes

Roberto Solimene



**Solid fuels (CLC of
solids,
oxicombustion,
annealing,
fragmentation)**

Osvalda Senneca



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