Imperial College
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An overview of Carbon Capture and Storage

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Summary

(1) CCS is a valuable tool in the fight against climate change

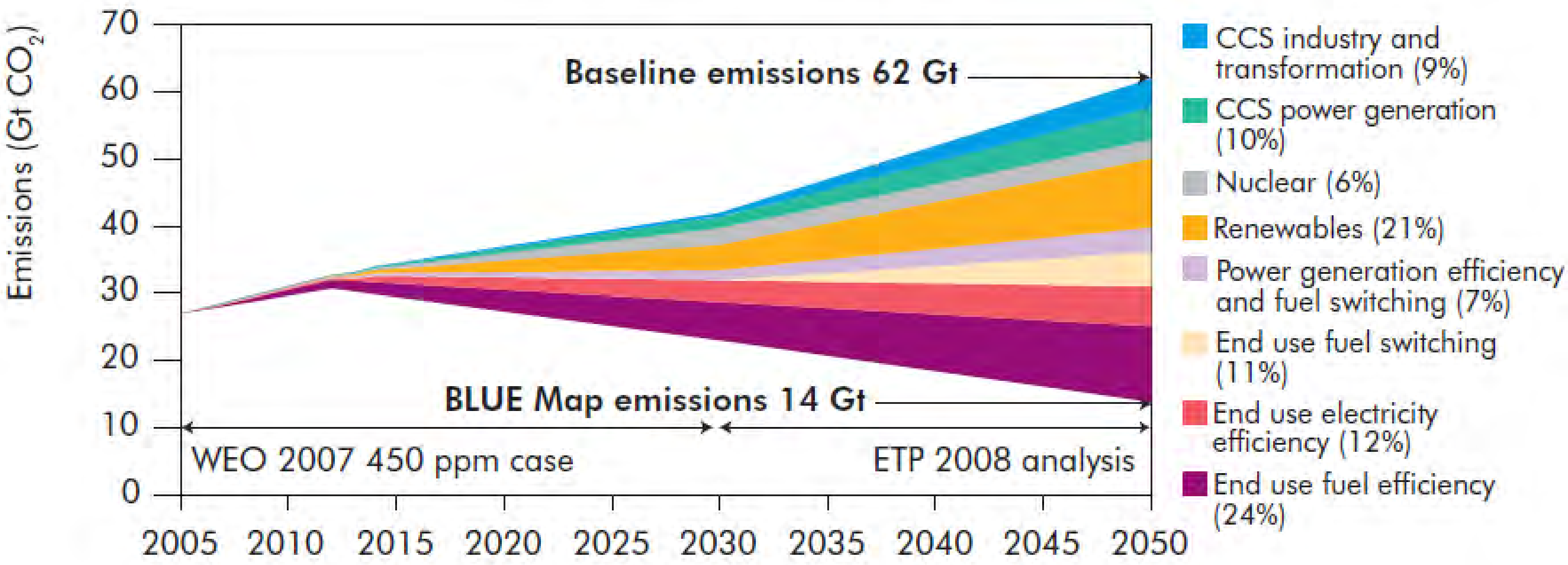
(2)High Temperature Solid Looping Cycles offer an efficient and low-cost alternative to traditional separation processes

(3) Key to this efficiency is integration to the power cycle(s) operated

(4)Start with a thermodynamically efficient system and optimise that…

(5)CO_2 reutilisation is an interesting exercise, but I have yet to be convinced that it is scalable.

CCS on Industry – very large.



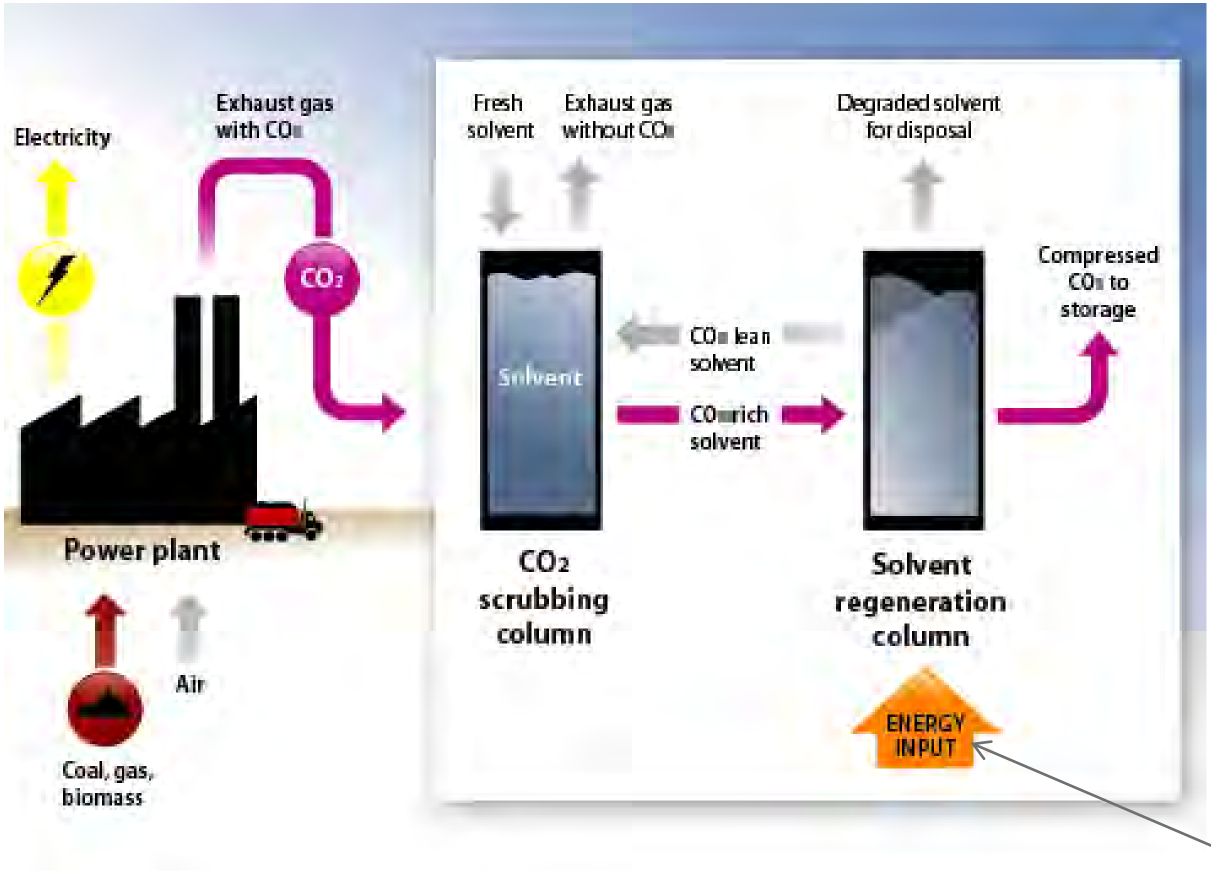
Around 20 % of the reductions in emission under the IEA blue map scenario.

Source: Energy Technology Perspectives 2008

Analyses conducted by Electric Power Research Institute indicate that without CCS, electricity prices increase by 210 % by 2050.
With CCS, the cost rise is 80 %.

Current Technology

Post-combustion capture – easiest to retrofit

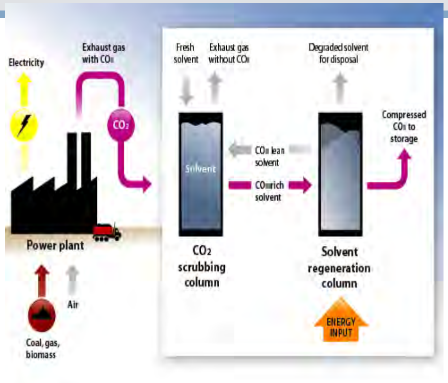


‘End of pipe technology’, can be retrofitted

Heat input for regeneration of solvent accounts for decrease in process /cost efficiency

Can be used on industrial processes other than power generation.

Technical and Environmental Issues – post combustion



Problems with the use of Amines for CCS*

Efficiency penalty!

Volatility of the amine solution (losses of amine from the system).

Corrosion of the stripper.

Degradation of the solvent (oxidative, thermal and with sulphur).

Effects on the ability of the power station to react to changes in demand?

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*An overview of CO_2 capture technologies
Niall MacDowell,[ab] Nick Florin,[a] Antoine Buchard,[c] Jason Hallett,[c] Amparo Galindo,[b] George Jackson,[b] Claire S. Adjiman,b Charlotte K. Williams,c Nilay Shahb and Paul Fennell*a
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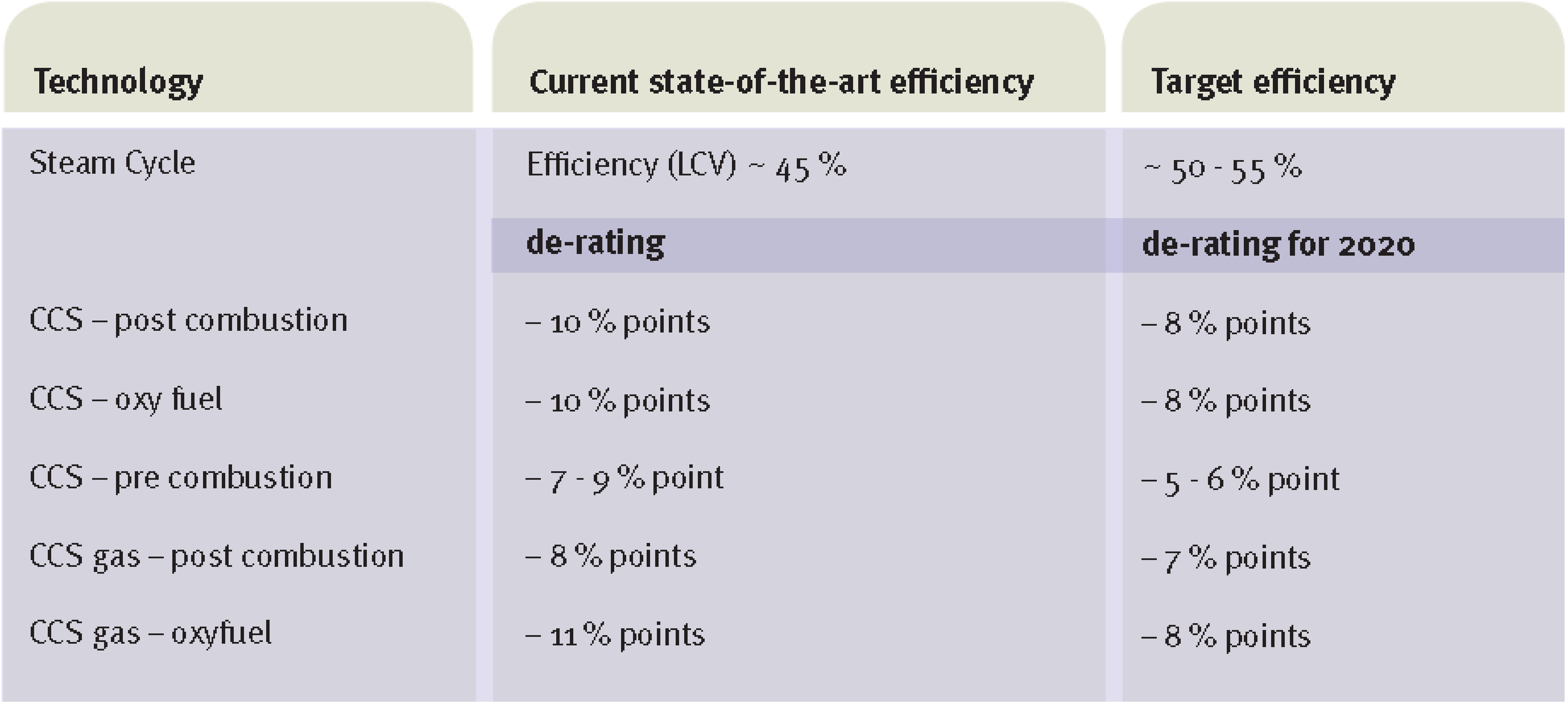
Reducing the efficiency penalty

Table. Efficiency estimates for capture and compression (published by IEA)



Technology	Current state-of-the-art efficiency	Target efficiency
Steam Cycle	Efficiency (LCV) ~ 45 %	~ 50 - 55 %
	de-rating	**de-rating for 2020**
CCS – post combustion	– 10 % points	– 8 % points
CCS – oxy fuel	– 10 % points	– 8 % points
CCS – pre combustion	– 7 - 9 % point	– 5 - 6 % point
CCS gas – post combustion	– 8 % points	– 7 % points
CCS gas – oxyfuel	– 11 % points	– 8 % points

Ca looping – 6 % including compression
Chemical Looping – 3 % (only compression)

2^{nd} Generation Technologies

Key differentiation – better thermodynamic integration with power cycle, when CCS is included.

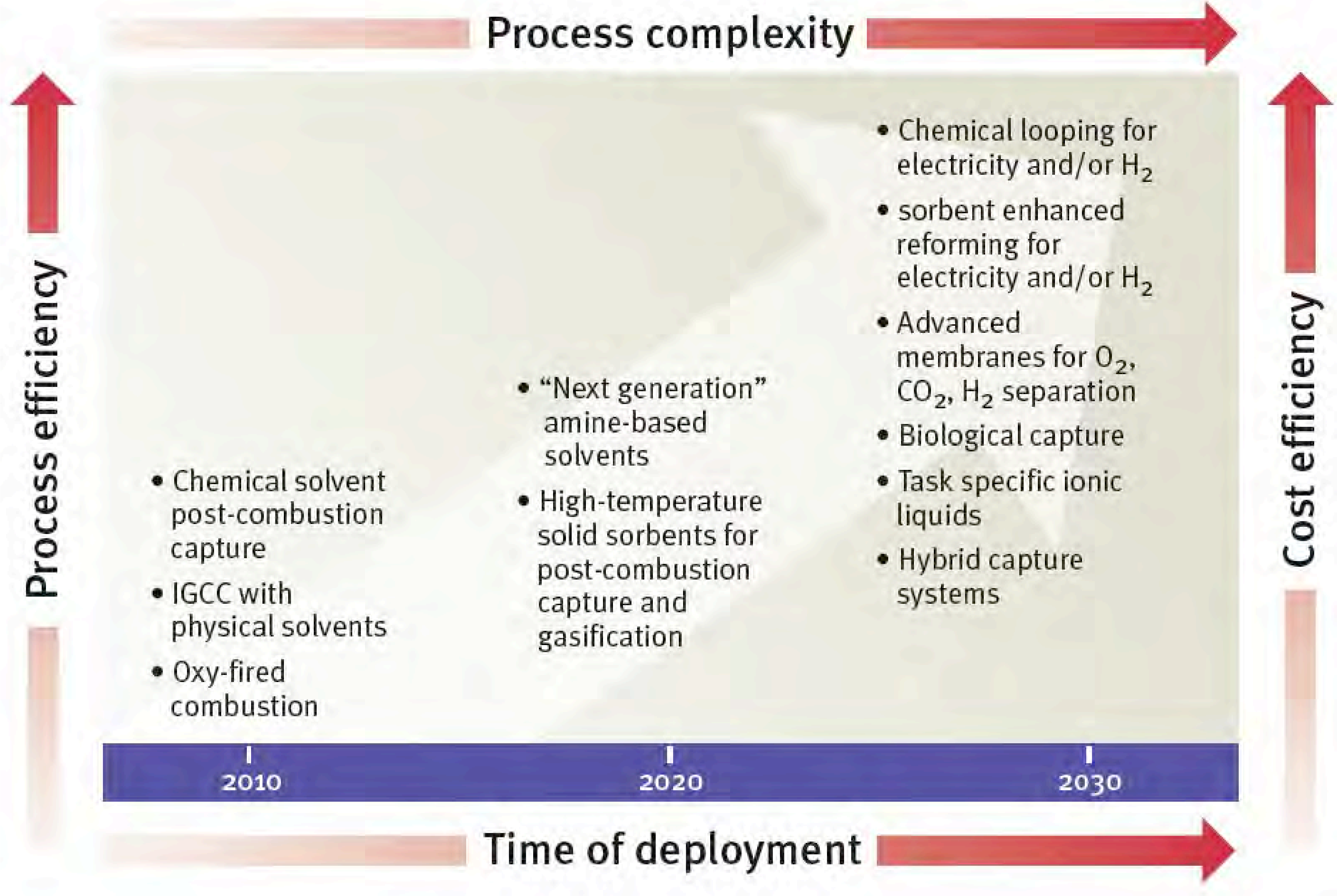
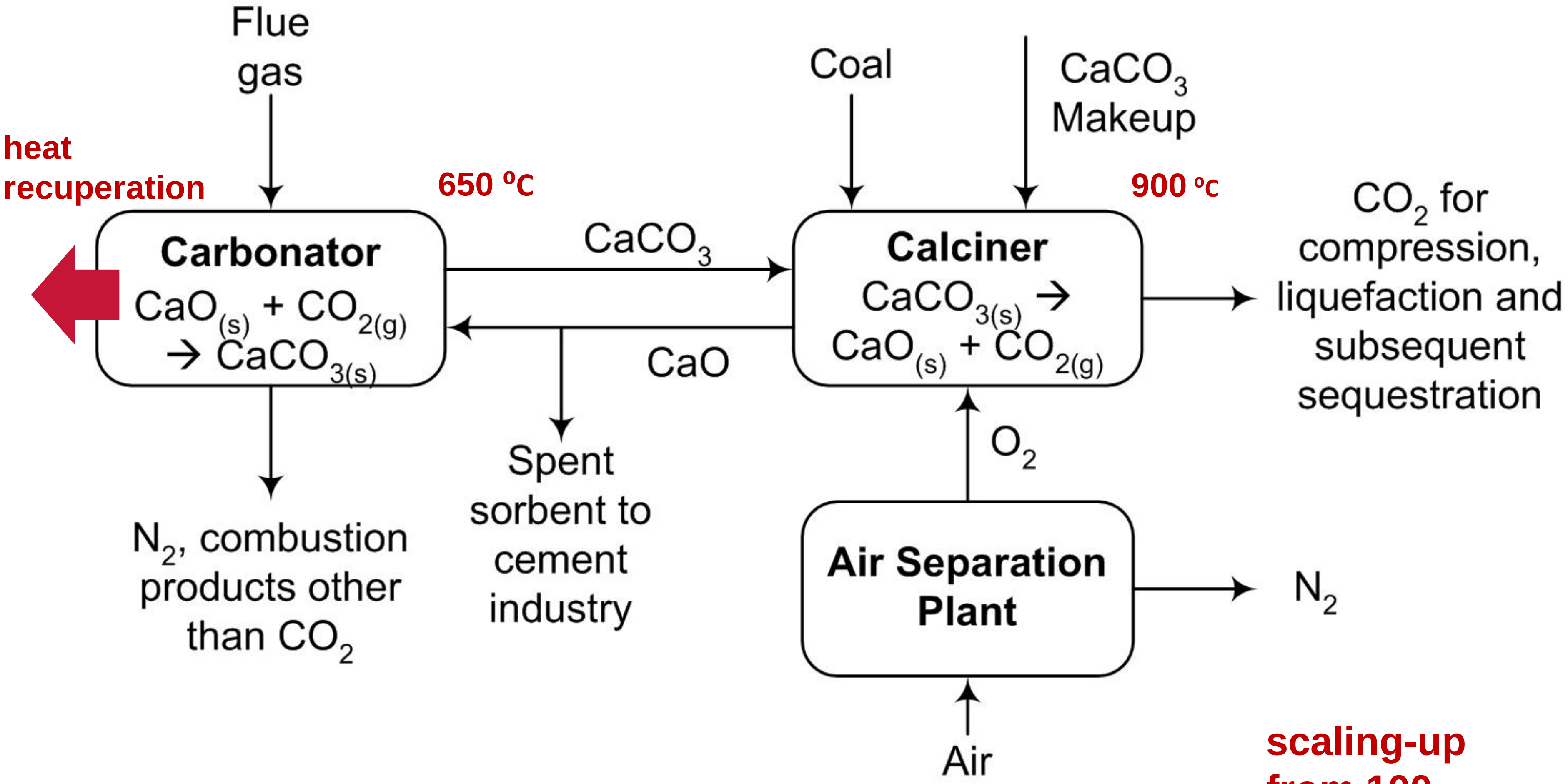


Figure. Likely technology adoption trajectory after Figueroa et al (2008)

E.g.:

Novel Technologies will be coming online soon



E.g. as proposed by Shimizu et al, 1999

scaling-up from 100 KW$_{th}$ to 1 MW range

Advantages

- Cost – numerous independent studies[1-4] show costs of £8 – 15 for the technology
- Spent sorbent can be used directly in cement manufacture[5]
- Intrinsic SO_2 capture

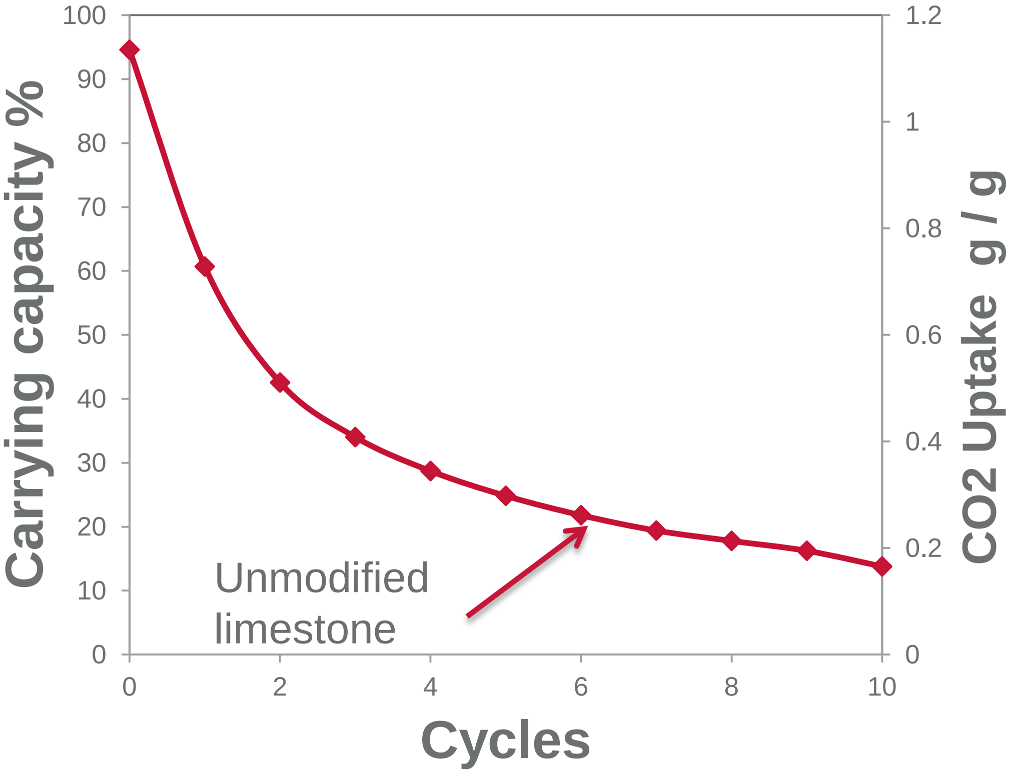
1. ***John S. Dennis**, University of Cambridge, UK*
   Chemical Looping Processes for Carbon Separation, 11 – 15th September 2011, Sardinia, Italy
2. *MacKenzie, A., et al., Economics of CO2 Capture Using the Calcium Cycle with a Pressurized Fluidized Bed Combustor. Energy & Fuels, 2007. **21**: p. 920-926.*
3. *Romeo, L.M., et al., Oxyfuel carbonation/calcination cycle for low cost CO2 capture in existing power plants. Energy Conversion and Management, 2008. **49**(10): p. 2809-2814.*
4. *Romeo, L. M., D. Catalina, et al. (2011). "Reduction of greenhouse gas emissions by integration of Cement Plants, Power Plants and CO_2 Capture Systems." Greenhouse Gases Science and Technology **1**(1): 72-82.*
5. *Dean, C.C., D. Dugwell, and P.S. Fennell, Investigation into potential synergy between power generation, cement manufacture and CO2 abatement using the calcium looping cycle. Energy & Environmental Science, 2011.*

Disadvantages

- Deactivation of sorbent (but on a g / g basis, **unmodified limestone** takes up more CO_2 than most carbon-based adsorbents – **when fully degraded**).
- Still requires ASU for calciner. See new UKCCSRC thermal oxygen project for solution.

1. Galloy, A., et al., CO2 Capture in a 1 MWth Fluidized Bed Reactor in Batch Mode Operation, in 5th International Conference on Clean Coal Technologies, Zaragoza, Spain, 8th - 10th May. 2011.

Unmodified Limestone



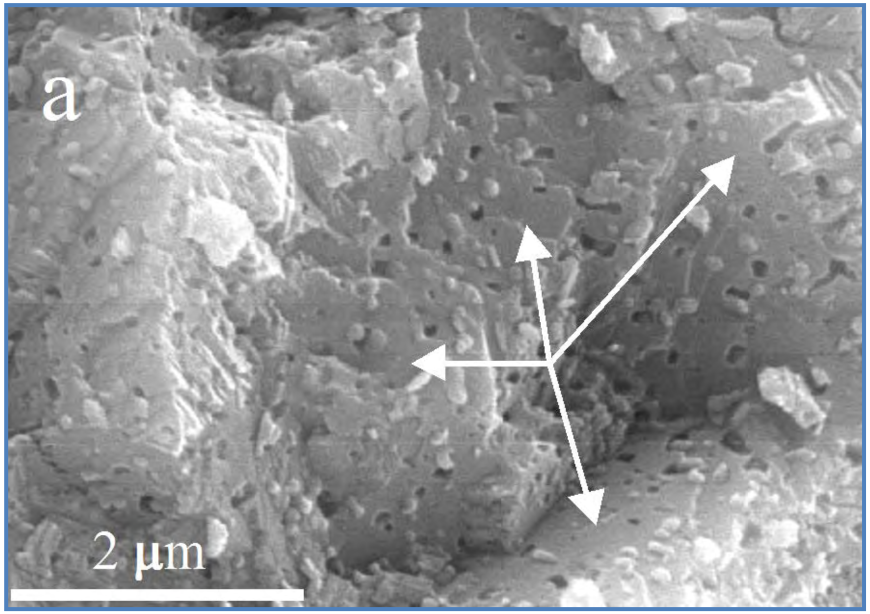
Unmodified limestone – decays rapidly

Now being tested in EU Caoling 1.7 MWth pilot plant

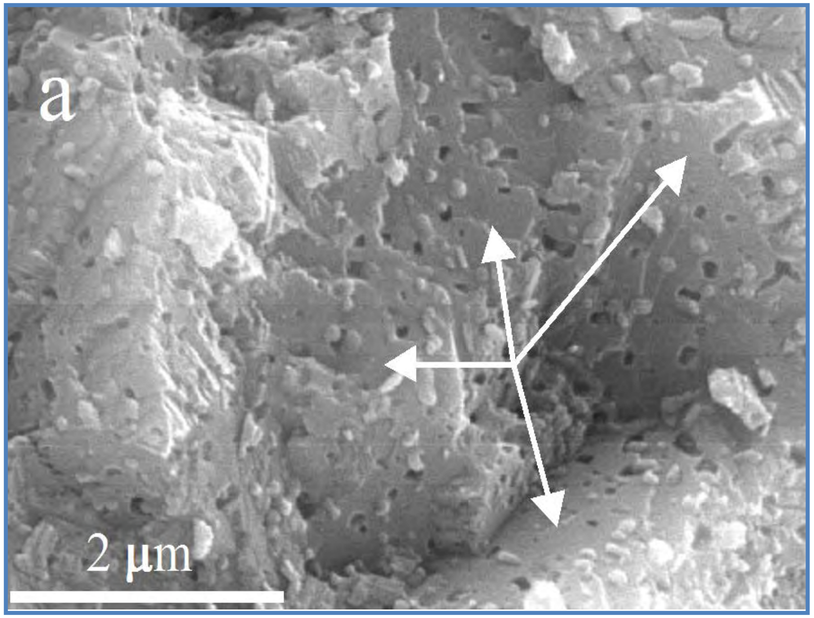
Note – unmodified limestone long term uptake ~ 0.16 g / g when fully degraded.

Sorbent reactivity decay

1
cycle



30
cycles



Abanades and Alvarez
Energy & Fuels, 2003

Initially – lots of pores in the 20 – 30 nm range
After multiple reactive cycles – small pores sinter into very large pores.

Main issues in real system:

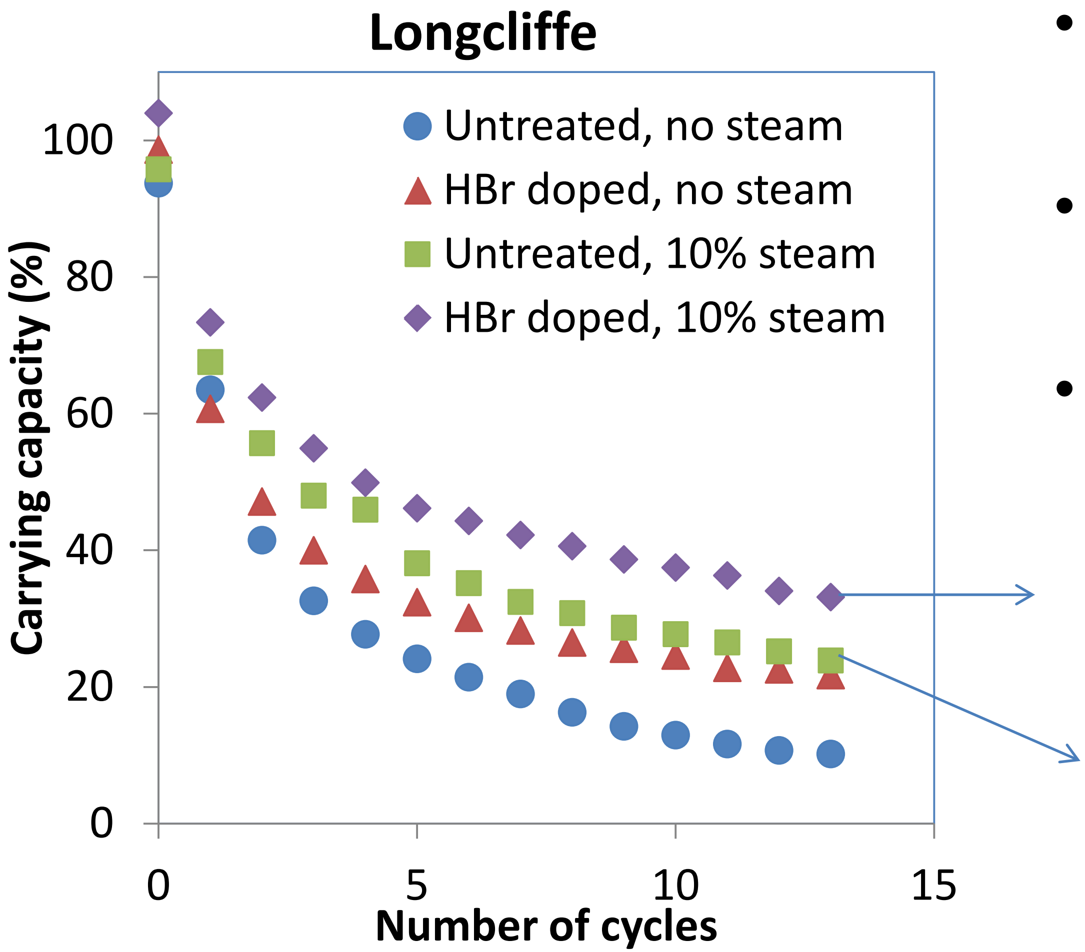
1. **sintering**
2. **attrition and fragmentation**
3. **competing reaction with sulphur**
4. **ash fouling in calciner**

Improvements to Natural Limestones

Why improve a natural limestone? Why not just produce an artificial sorbent?

Natural limestones are CHEAP. (£20 per tonne)
Natural limestones are easy to dispose of into cement manufacture.
Natural limestones are pretty good anyway.
There are diminishing returns in improving the reactivity beyond a certain level.

Additive Improvement in Performance: HBr Doping and Steam Presence

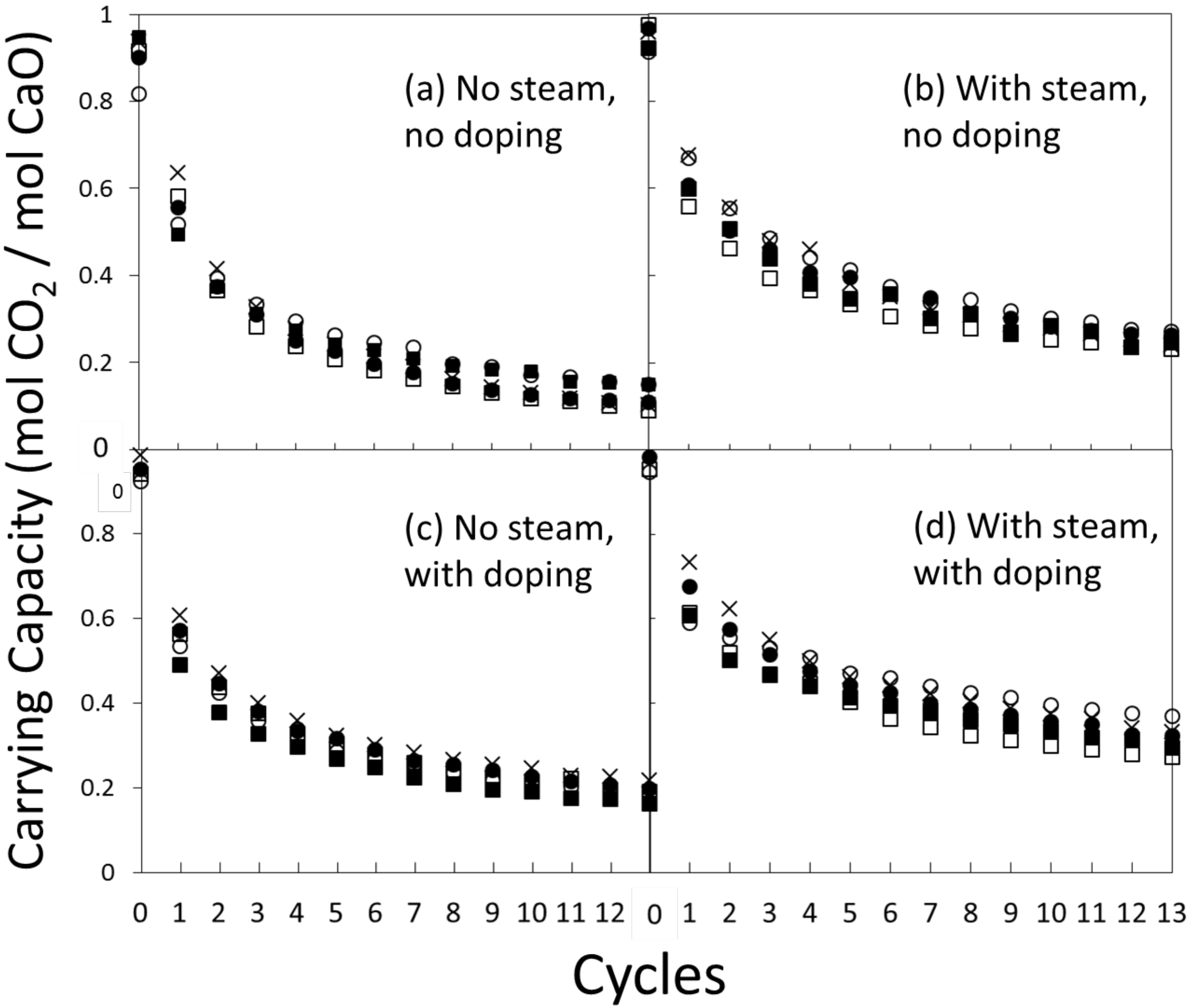


- HBr doping enhances performance of natural limestone
- Presence of steam enhances performance of natural limestone
- These effects are additive

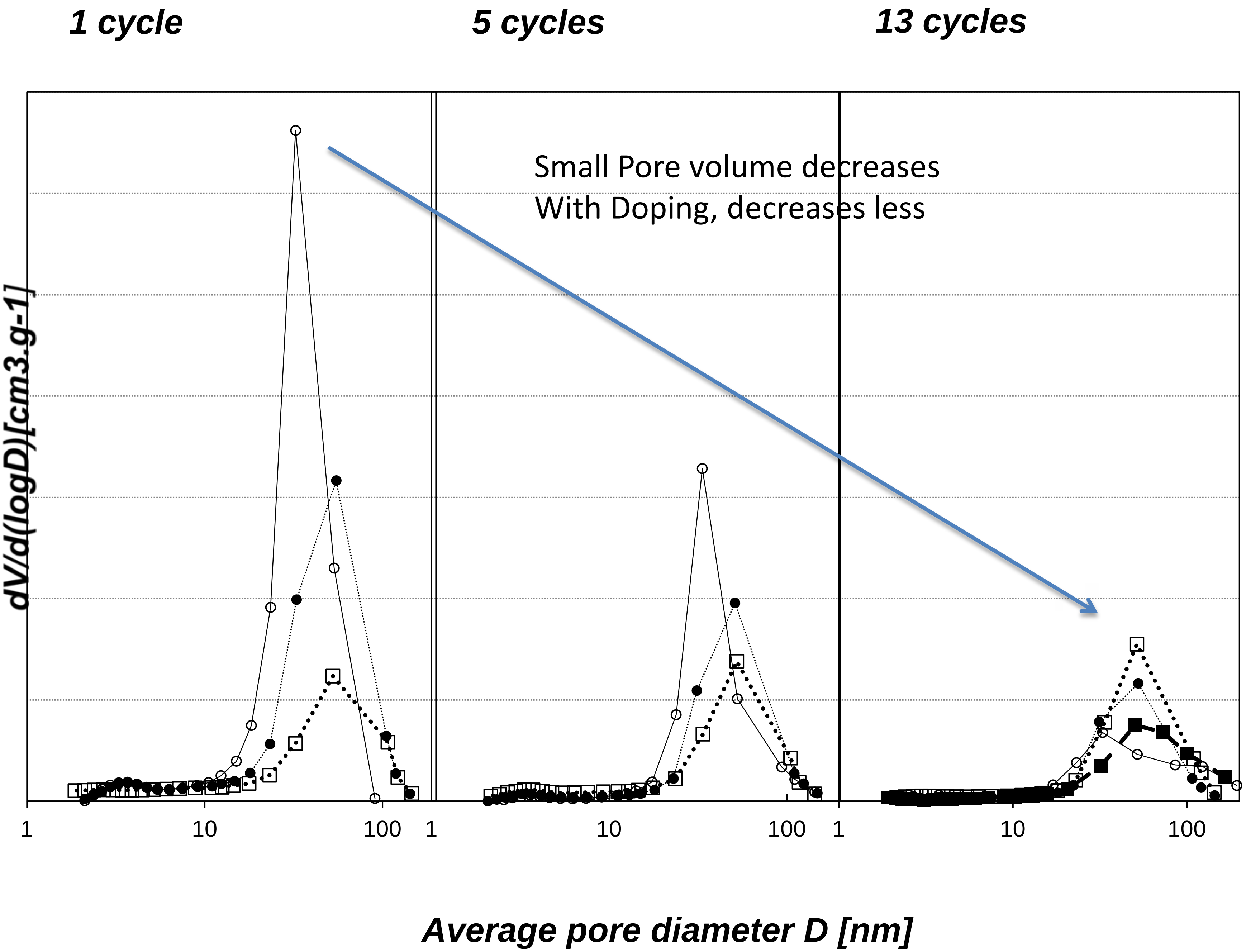
0.26 g CO_2 / g CaO or 5.9 mmol CO_2 / g

4.3 mmol CO_2 / g

Not bad for something you dig up out of the ground (£20 / ton)

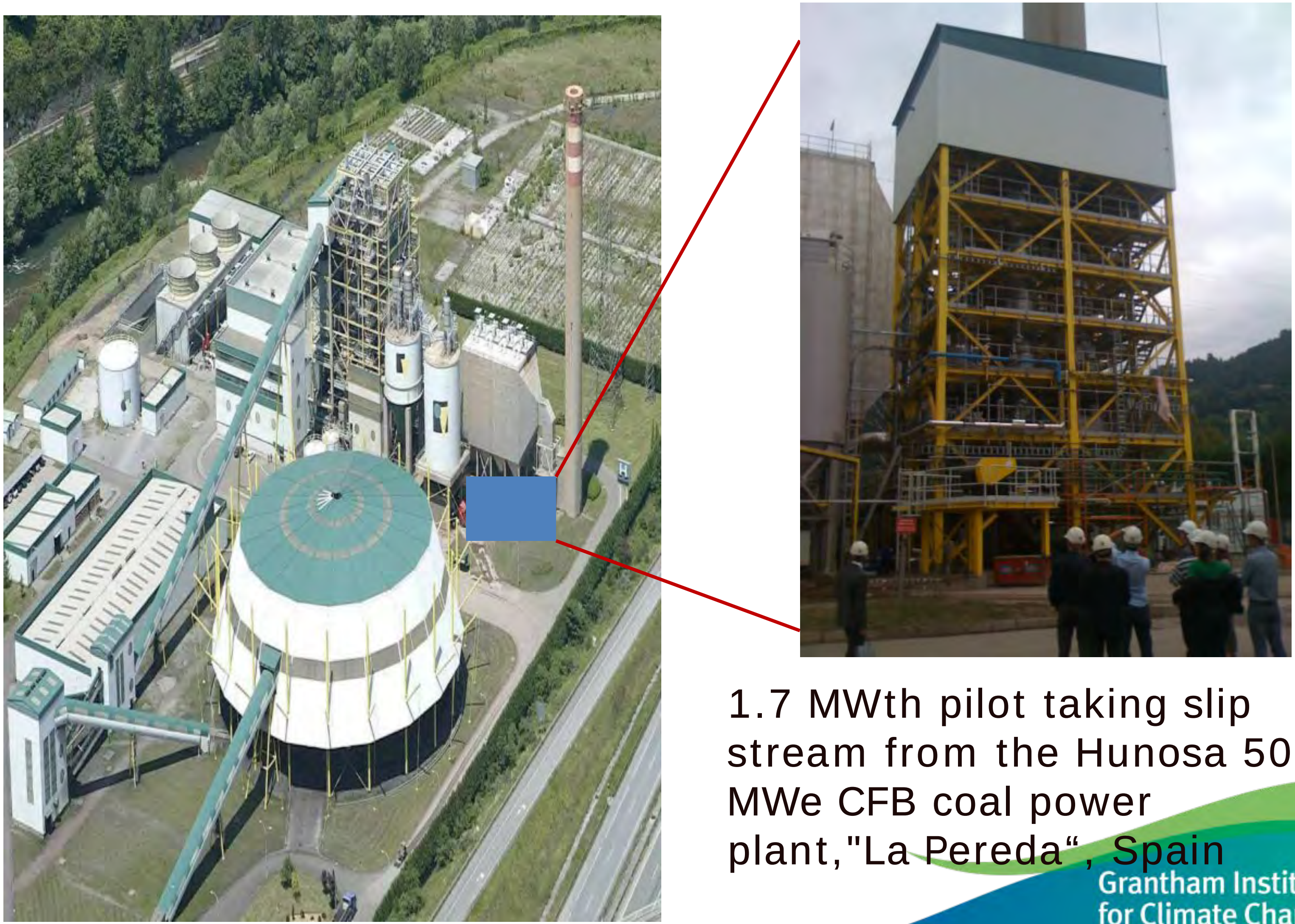


Works for numerous limestones

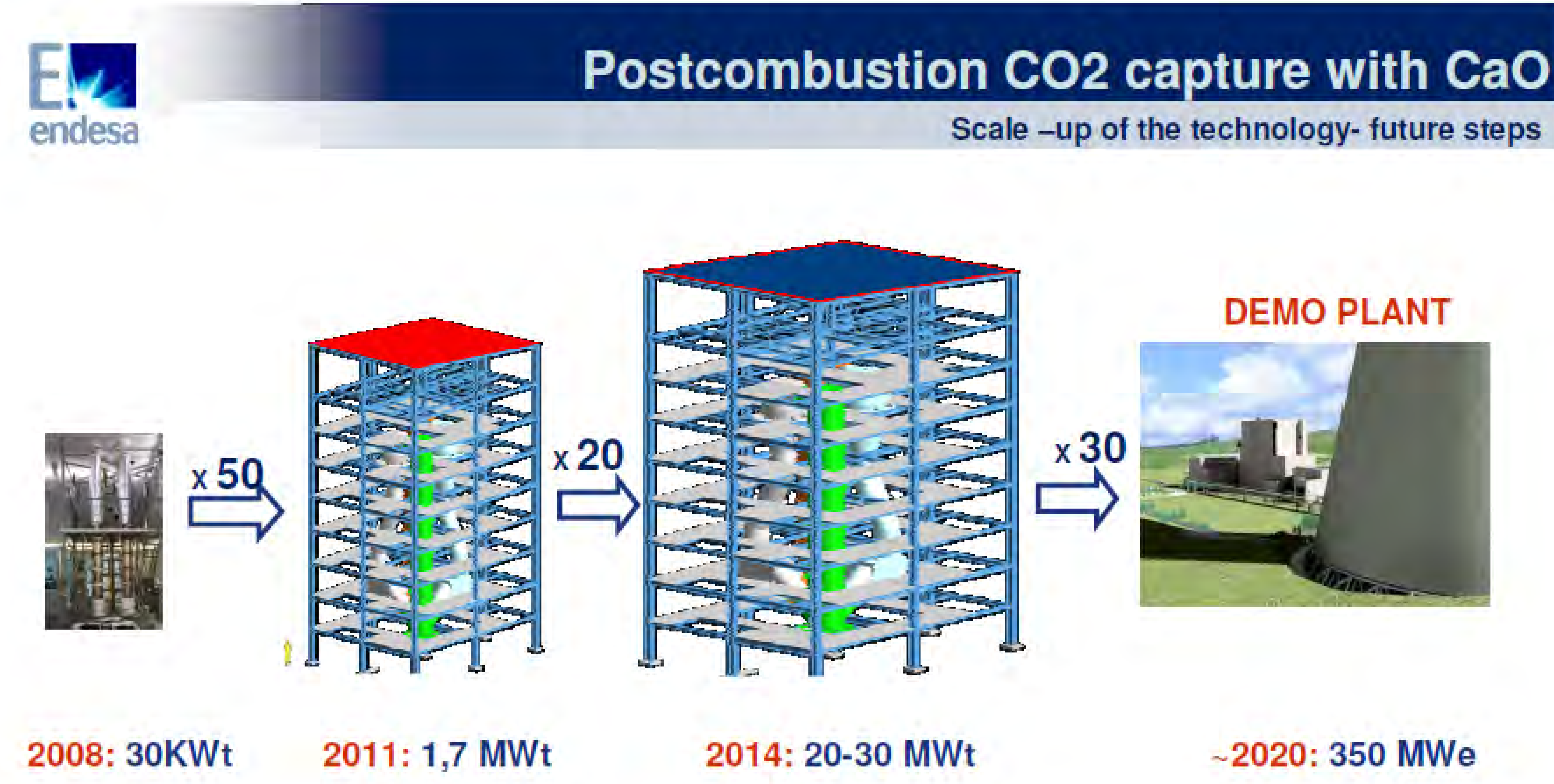


Small Pore volume decreases
With Doping, decreases less

Technology readiness level



1.7 MWth pilot taking slip stream from the Hunosa 50 MWe CFB coal power plant, "La Pereda", Spain



Postcombustion CO2 capture with CaO

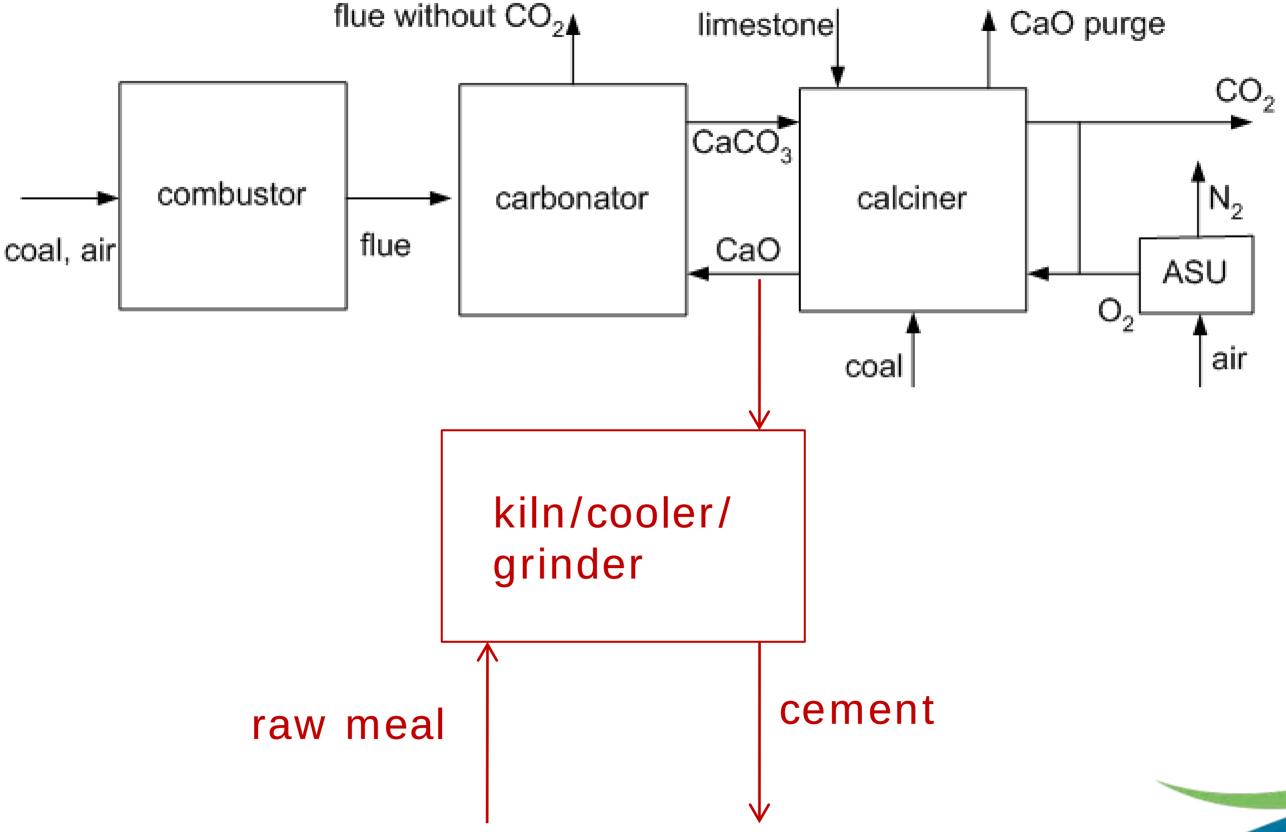
Scale –up of the technology- future steps

2008: 30KWt
2011: 1,7 MWt
2014: 20-30 MWt
~2020: 350 MWe

Which is easier to scale? A circulating fluidised bed, or an amine scrubbing tower?
FW is already offering a 800 MWe CFB system – with 460 MWe already operating in *Łagisza, Po*

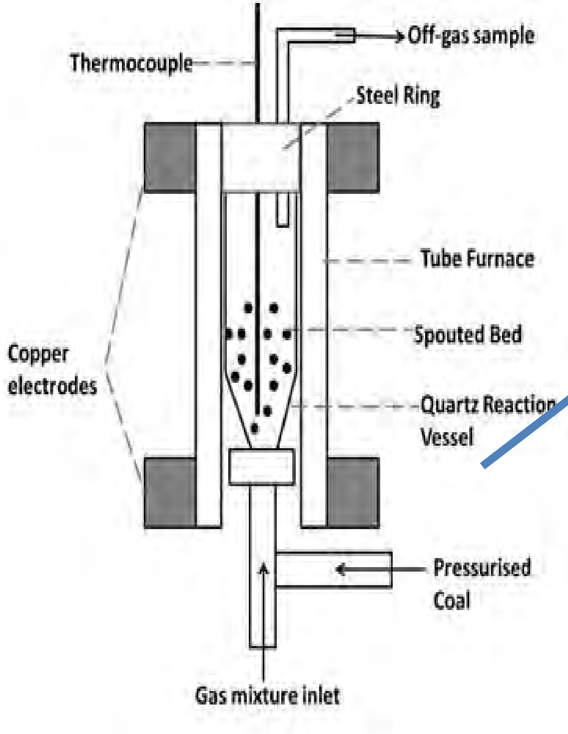
Also – don't forget 5 years of research pre 2003 at TGA / small scale BFB

Re-use spent sorbent in cement plant



Cement production using spent sorbent

3 kW spouted bed reactor



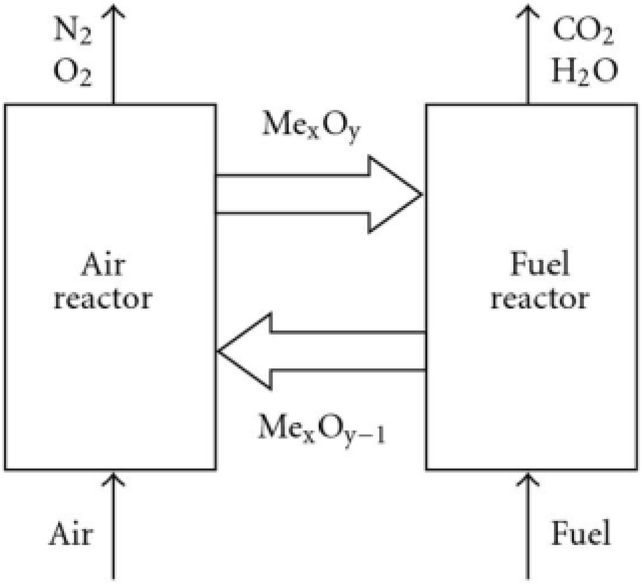
$CaO + SiO_2 + Al_2O_3 + Fe_2O_3$
ground, mixed and fired at 1450 °C

- This work used 'pure' oxides instead of typical raw materials (e.g. sand/clay) to allows any change in the concentration of trace elements in the sorbent to be measured
- No major issues observed with cement quality.

Dean et al. Energy and Environmental Science , 2011

Chemical Looping Combustion

Determining the effect and fate of sulphur in Chemical Looping Combustion



Similar to Calcium (carbonate) looping – Oxygen shuttled around instead of CO_2.

Fuel Reactor:

$$3Fe_2O_3 + CO \leftrightarrow 2Fe_3O_4 + CO_2; \qquad \Delta H^0_{298K} = -43.2\text{kJ/mol}$$

$$3Fe_2O_3 + H_2 \leftrightarrow 2Fe_3O_4 + H_2O; \qquad \Delta H^0_{298K} = -2.7\text{kJ/mol}$$

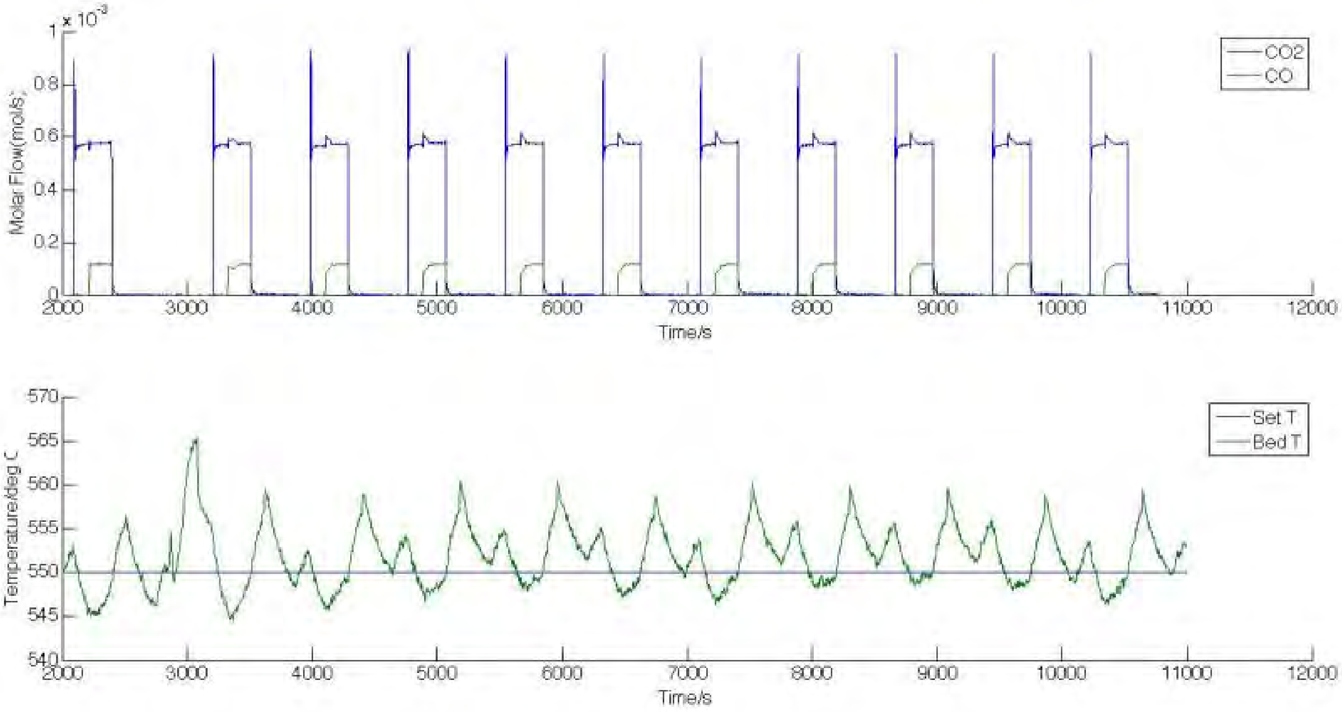
Air Reactor:

$$4Fe_3O_4 + O_2 + 3.762N_2 \leftrightarrow 6Fe_2O_3 + 3.762N_2; \qquad \Delta H^0_{298K} = -479.5\text{kJ/mol}$$

Chemical Looping Combustion

- A solid transfers oxygen to the fuel
- N_2 from the air never mixes with the fuel
- No separation of N_2 / CO_2 required at the end.
- INTRINSIC separation – very low efficiency penalty).
- High temperature system

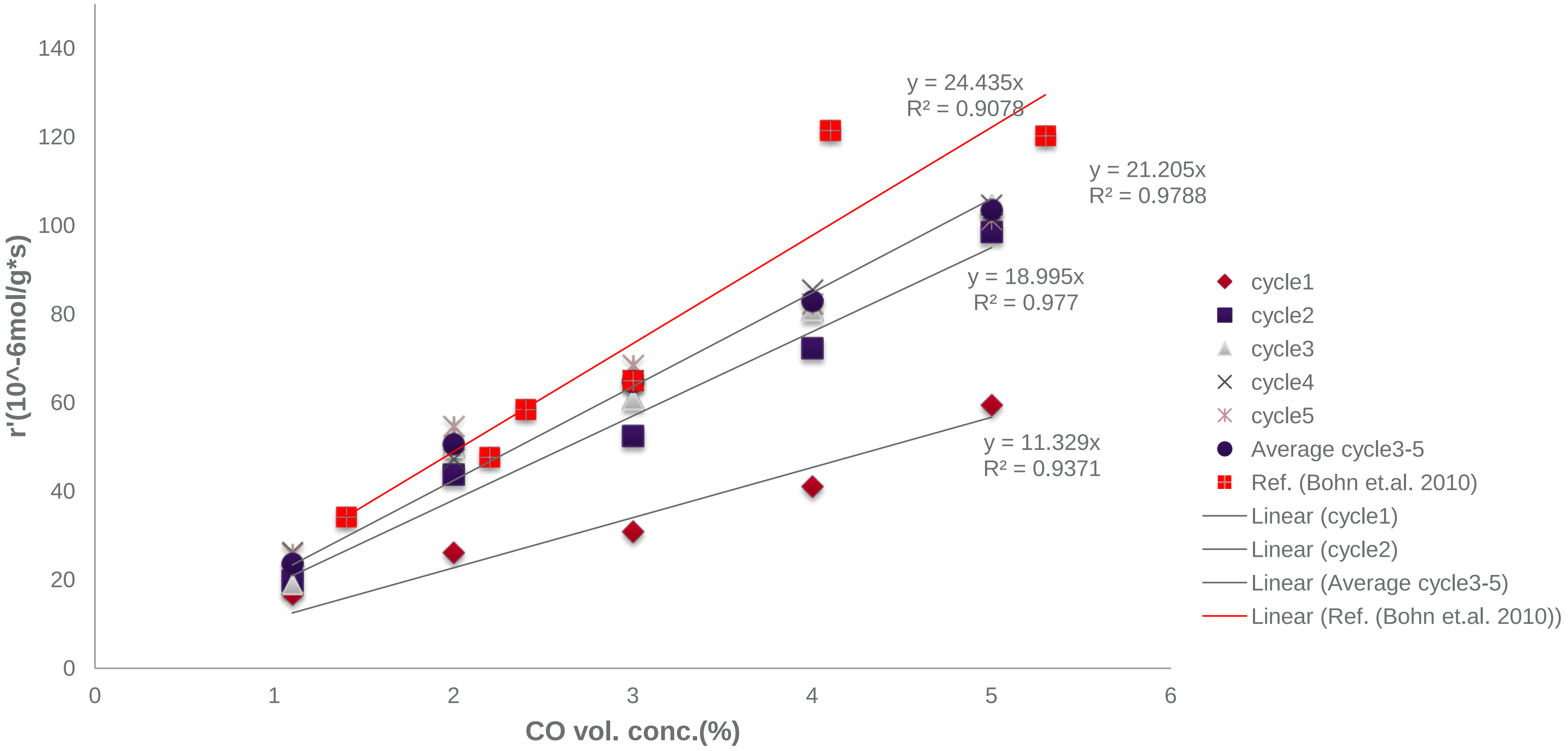
A 10 Cycle Experiment of Iron oxide reduction with CO at 823K, 3 vol% CO (180s reduction, 240s oxidation)



Nice, easily reversible reaction

Research focuses on enhancing particle properties (particle engineering) and reducing the cost of the CLC compounds.

Dependence of overall rate of Fe_2O_3 reduction on CO conc. at 823K



*Here the maximum rate of CO was taken as overall rate while extrapolated initial rate was taken as overall rate in the literature.

Chemical and Carbonate Looping Combustion

Both technologies have significant future potential for the future – and this is demonstrated by both technical feasibility, systems and **economic analysis**

•Both technologies are moving to scale (1 – 2 MWth) – they are <u>not</u> laboratory curiosities.

•Research on oxygen / CO2 carriers is still important – selectivity, activity, longevity, cost, ability to

manufacture, fuel – carrier combinations vs. natural/synthetic carriers …

•However, both technologies could be built today and would have significantly better efficiency than “first generation” technologies.

Other technologies

Chilled ammonia

Alternative chemical solvent scrubbing technology for post-combustion capture using ammonia/ammonia carbonate

Advantages

(i) Alstom is developing a chilled ammonia process which reportedly uses only15 % of the amount of steam consumed using MEA for regeneration
(ii) Relatively high CO_2 carrying capacity (i.e. more CO_2 is captured per gram of solvent)
May be even more efficient at locations where cold cooling water is available (iii) to minimise energy needed for refrigeration

Disadvantages/ technical challenges

(i) Requires electricity for chilling – overall capture efficiency only marginally better than amine scrubbing

“Next generation” amine based sorbents

Amines supported on high-surface area solid supports

Advantages

(i) potential to improve overall efficiency because they avoid some of the thermal penalty associated with the use of aqueous-based amine systems
(ii) commercially available soild amines used for many years for CO_2 removal from closed environments, e.g. space shuttles and submaries
(iii) a lot work done in the USA with funding from the US DOE/NETL, e.g., amines grafted onto high surface area zeolite supports

Disadvantages/ technical challenges

(i) Limited testing with realistic gases
(ii) low capacity for CO_2: The maximum CO_2 capture capacity recently reported was 0.132 g-CO_2/g-sorbent (which reduces to about 0.101 g CO_2/g under realistic conditions), compared to about 0.157 g-CO_2/g-sorbent for CaO

Ionic liquids

A broad family of salts consisting with an organic cation bonded to either an organic or inorganic anion

Advantages

(i) Physical solvents with the potential for low energy requirements associated with CO_2 release and regeneration
(ii) Remain stable at temperatures up to about 300 °C, which means the need for flue gas cooling prior to CO_2 capture may be avoided.
(iii) SO_2 solubility has also been demonstrated, thus offering the potential to integrate the sulphur removal step

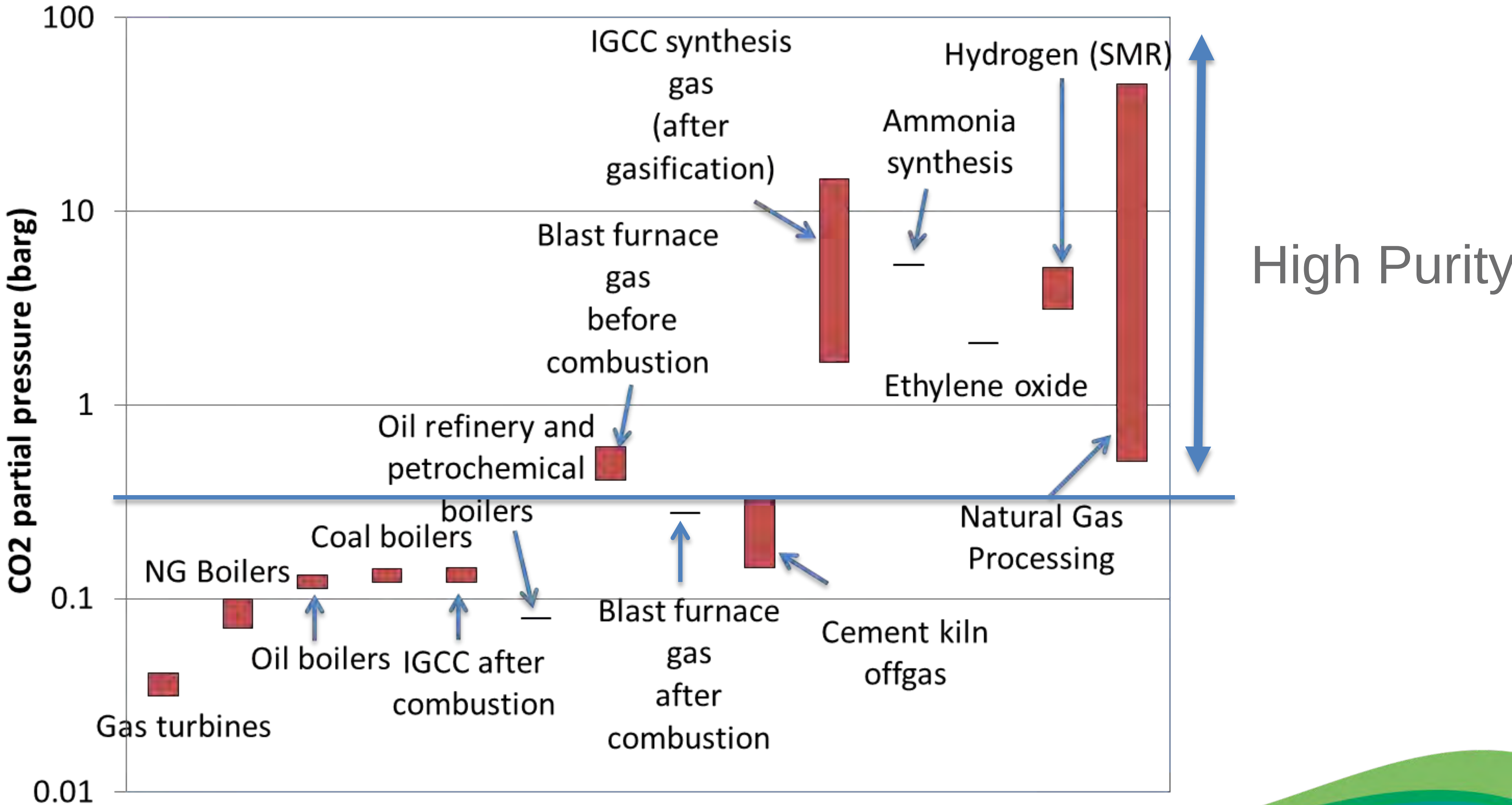
Disadvantages/ technical challenges

(i) A number of ionic liquids are commercially available, but have not been optimised for CO_2 solubility.
(ii) Currently prohibitively expensive (order of $1000 / kg) – watch this space… Chemical Engineers now involved!
(iii) Manufacturing process is very complicated

Technology readiness levels (TRL)… author’s opinion based on literature survey and publicly available data

Technology	**TRLs**
Post combustion capture with MEA	6
IGCC with physical solvents (e.g. Rectisol process)	6
Oxy-combustion	5
Post-combustion carbonate looping	4–5
Chemical looping combustion	4
Sorbent enhanced reforming	3–4
Post-combustion with algae	3–4
Post-combustion capture with “second generation” sorbents, e.g.: supported amines, ionic liquids	2–3
Membranes for CO_2 capture	2–3
ZECA	1–2

Sources of CO$_2$ are variable in composition and pressure – one technology does not suit all



Future Horizons

Novel Technologies are in the process of being proven at pilot plant scale.

It is important not to stifle future competition by only focussing on the incumbent technologies.

Integration between industries may become increasingly important – both for co-utilisation of storage infrastructure and for flows of heat and material between industries.

Non power CCS accounts for a similar proportion of installed capacity (one “wedge” each) to CCS on power generation, but receives much less interest.

Might help in 2020. Critical for long-term mitigation.

“Future”

Technologies which show promise

- Ionic Liquids – potentially eliminates problems with solvent losses (but problems with viscosity and very high molecular mass).
- Methane reforming / water gas shift / CO_2 capture (but how to integrate with power generation)
- New technologies for O_2 separation (uncoupled chemical looping, membranes, etc).
- Links between CCS and renewables (solar thermal / carbonate energy storage).
- CO_2 capture from the air?
- CO_2 + Hydrogen = methanol?
- Carbon utilisation?
- Mineralisation?

CO_2 capture From the Air

- It is possible to capture CO_2 direct from the air
- It is possible for me to generate electricity with a hand crank
- Is it a good idea?
- Is it scalable?
- Should we ask people other than the purveyors of the technology to do independent analysis?
- How likely is it that a technology which now costs $250,000 per unit will cost $25,000 with economies of scale?
- **Heath and Safety, efficiency**, **LCA**?
- Is it easier to take water from a river or to condense it out from the air?
- Claims of efficiency often rely on minimal stripping of air – 1 ppm removed...

THERMODYNAMICS!

CO$_2$ Re-utilisation

USA ONLY

Source	Annual CO2 production (MtCO2)	Percentage of Total Emissions
Power	2530	84.0%
Refineries	154	5.1%
Iron & Steel	82	2.7%
Gas Processing	77	2.6%
Cement	62	2.1%
Ethylene	61	2.0%
Ethanol	31	1.0%
Ammonia	7.8	0.3%
Hydrogen	6.8	0.2%
Ethylene Oxide	1.2	0.0%
TOTAL	**3013**	**100%**

Global ~ 10 x USA emissions

GLOBAL

Process	Global Annual CO2 Usage	Typical source of CO2 used	Lifetime of storage
Urea	65-146Mt^	Industrial	6 Months
Methanol	6-8Mt	Industrial	6 Months
Inorganic Carbonates	3-45Mt #	?	Decades
Organic Carbonates	0.2Mt	?	Decades
Polyurethanes	10Mt	?	Decades
Technological	10Mt	?	Days to Years
Food and drink	8Mt	?	Days to Years
TOTAL	**102 – 227Mt**		

Notes:

^, # The demand for CO2 in Urea and Inorganic Carbonate production is particularly uncertain. Various sources have quoted figures with orders of magnitude differences.

Sources outweigh sinks by several orders of magnitude (more than a factor of 100).

The storage of CO$_2$ is frequently short term.

The huge volume of CO$_2$ produced means that any by-product of CO$_2$ at the scale required to make a difference in climate terms will immediately saturate the market.

The use of CO$_2$ as a novel feedstock is a good idea if it is justified by the economics – but will not have significant climate benefit, particularly if the storage is short term.

$CO_2 + 3\ H_2 = CH_3OH + H_2O$

- Production of liquid fuels from “excess” or “free” renewable energy
- Is there such a thing?
- There is always an opportunity cost – always something else which can be done.
- Is this an efficient way to store the electricity?

THERMODYNAMICS!!!

Methanol Production and Use

	Efficiency
H2 from water	50%
H2 + CO2	80%
Use of fuel in ICE	30%
Overall	**12%**

Electric Vehicle

	Efficiency
Pumped hydro	70%
Battery charging[1]	90%
Electric Vehicle	90%
Overall	**57%**

	Efficiency
Battery[1]	90%
Electric Vehicle	90%
Overall	**81%**

What is the capacity factor for equipment relying on “free” renewable energy? Won’t the power systems engineers be trying to minimise this?

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[1] Stevens, J.W. And Corey, G.P. A study of lead-acid battery efficiency near top-of-charge and the impact on PV systems design. Photovoltaic specialists conference, 1996. 13 – 17 May 1996, Washington DC, USA.

Mineralisation

- Securely locks away CO_2 by reaction with rocks such as serpentine to produce carbonate rocks
- 3 – 6 times more rock required to be mined than the coal from which it is capturing the CO_2 (basic mass balance)
- Needs to be ground to <100 microns before reaction – electricity use very significant[1]
- Reaction slow – massive reactors
- 100 tonne railway carriage of acid / stone sludge produced every 8 minutes for a 500 MWe power station.
- What else could we do with the resources deployed for this mining?
- My opinion: Not a viable technology for power stations but does have niche applications in waste / residue treatment.

[1] *Strubing, MSc, Imperial College, 2007.*

Conclusions (CCS)

(1) The pace of deployment required for CCS is very fast

(2)CO_2 capture technologies are currently expensive and impose high efficiency penalties on power stations.

(3)New technologies will be coming online soon. These are frequently referred to as 2nd generation technologies – but where are the first generation technologies?

(4) The technology is generally applicable to a number of different sources, including industrial emissions, and not just power generation.

(5)Personally, I have yet to be convinced by CO_2 utilisation for anything other than enhanced oil recovery.

Acknowlegements

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Staff and Fellows of the Grantham Institute.

[1]Imperial College London

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