The Future of Ca Looping Technology

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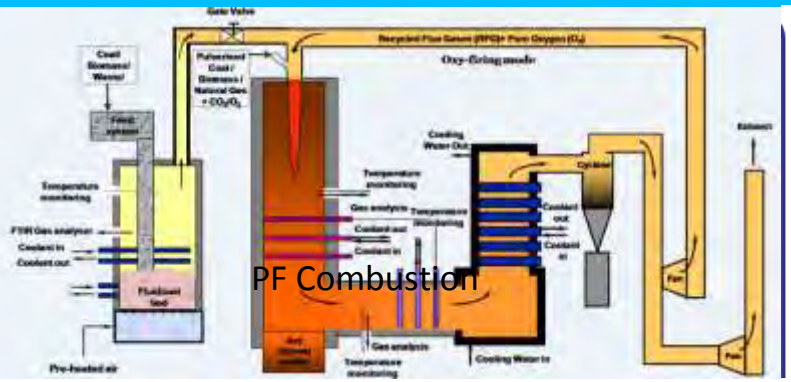
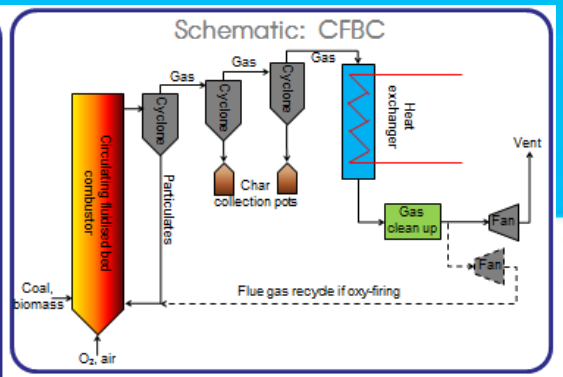
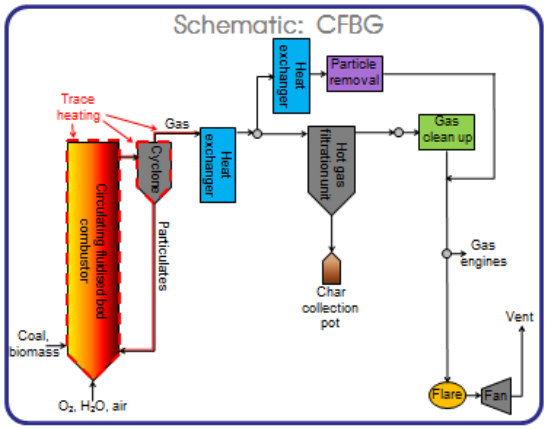
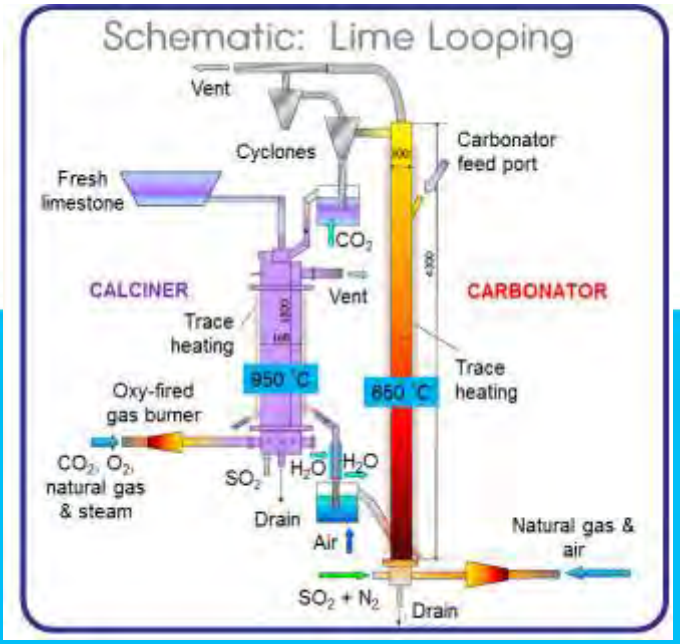
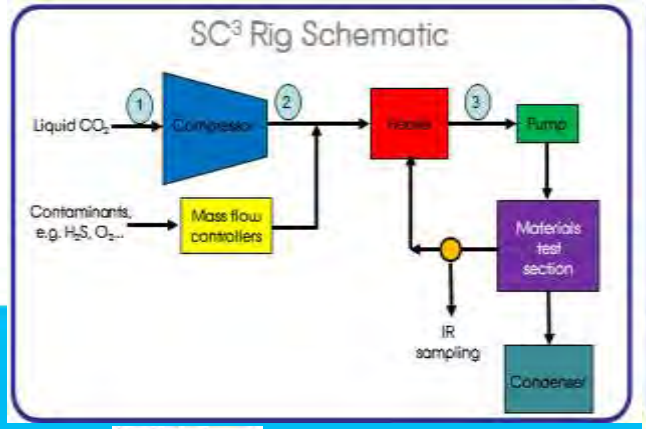


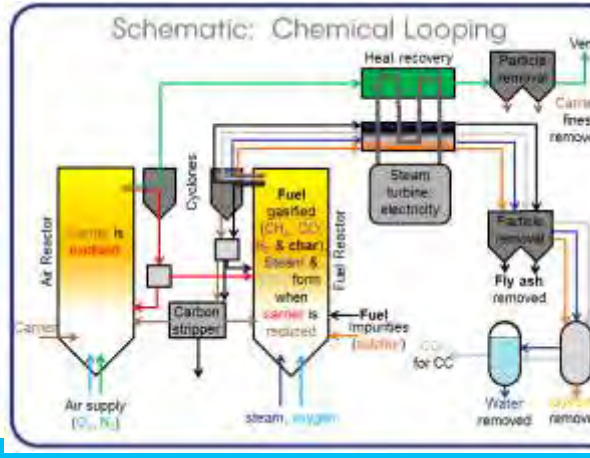




Pilot Scale Plant at Cranfield's Centre for Combustion and CCS







Estimate of Potential CO_2 Emission Reductions by CCS from Industry in Europe (based on ZEP 2013)

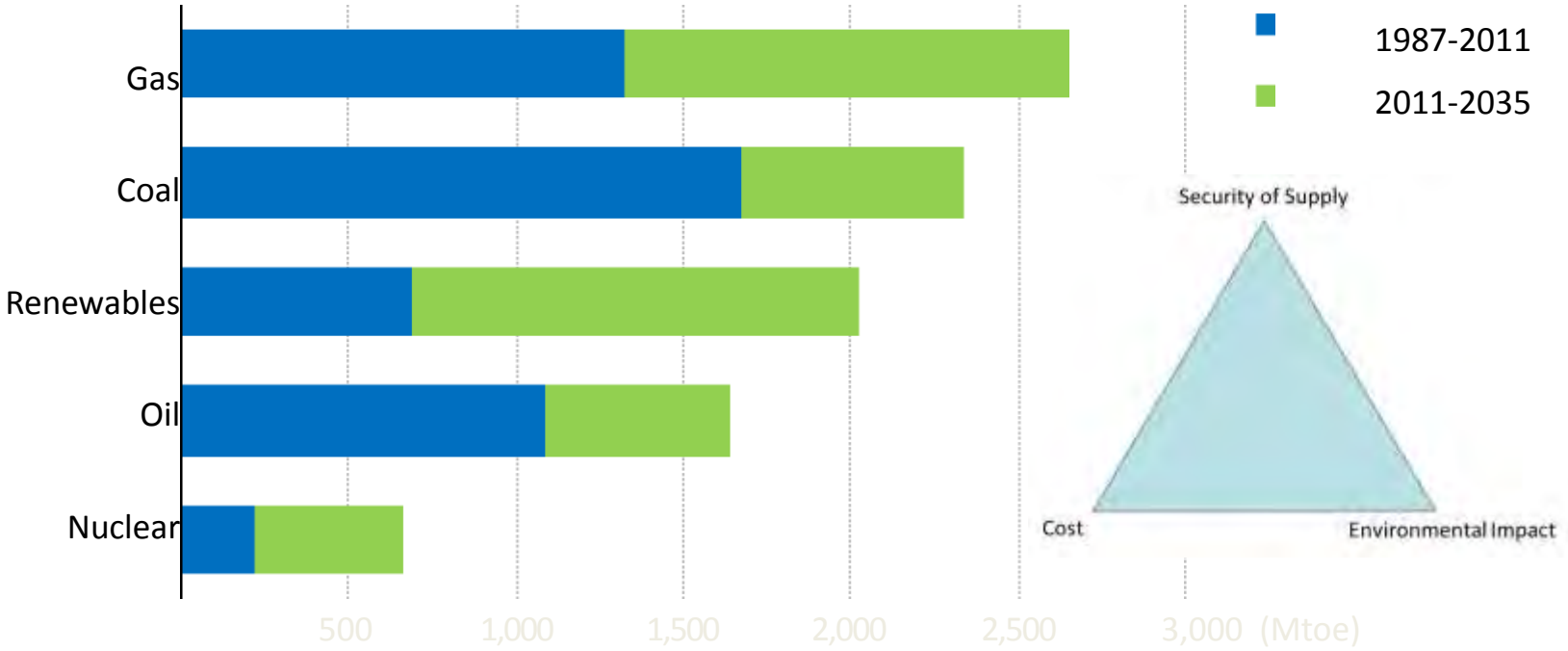
Sector	Assumption for estimate	CO_2 emission reduction, Mtpa
Iron and Steel	50% of emissions from blast furnaces captured	89
Cement	50% of emissions from cement plant captured	50
Refineries	Most emissions from hydrogen production captured, some emissions from combustion plant captured, totalling 25%	33
Chemicals	Available (western Europe) ammonia plant emissions captured, 80% cracker emissions captured, 10% combustion emissions captured	36
Total		208

Author: Dr Peter Brownsort, Scientific Research Officer
Scottish Carbon Capture & Storage (SCCS)

A mix that is slow to change

WORLD ENERGY OUTLOOK 2013

Growth in total primary energy demand



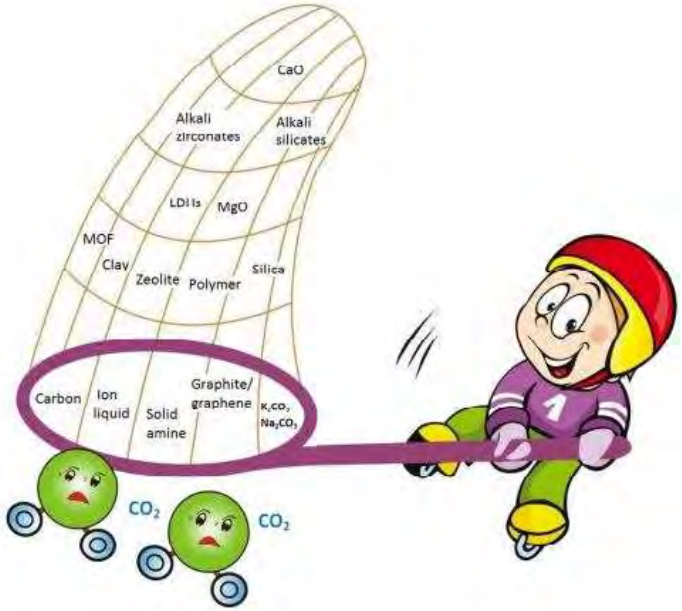
Today's share of fossil fuels in the global mix, at 82%, is the same as it was 25 years ago; the strong rise of renewables only reduces this to around 75% in 2035

© OECD/IEA 2013

Ca and CLC Future Technologies?

- A critical issue is deciding which technologies have a future and which do not and under what conditions – Solid fuels like coal, or gas?
- If you make H_2 from what source & how do you use it?
- Lots of R&D and papers, but are they making a significant difference and which ones make the difference?
- Ca and CLC are the newest of the contenders

Selecting the winners!



Wang et al, Envir Sci & Tech, 2014

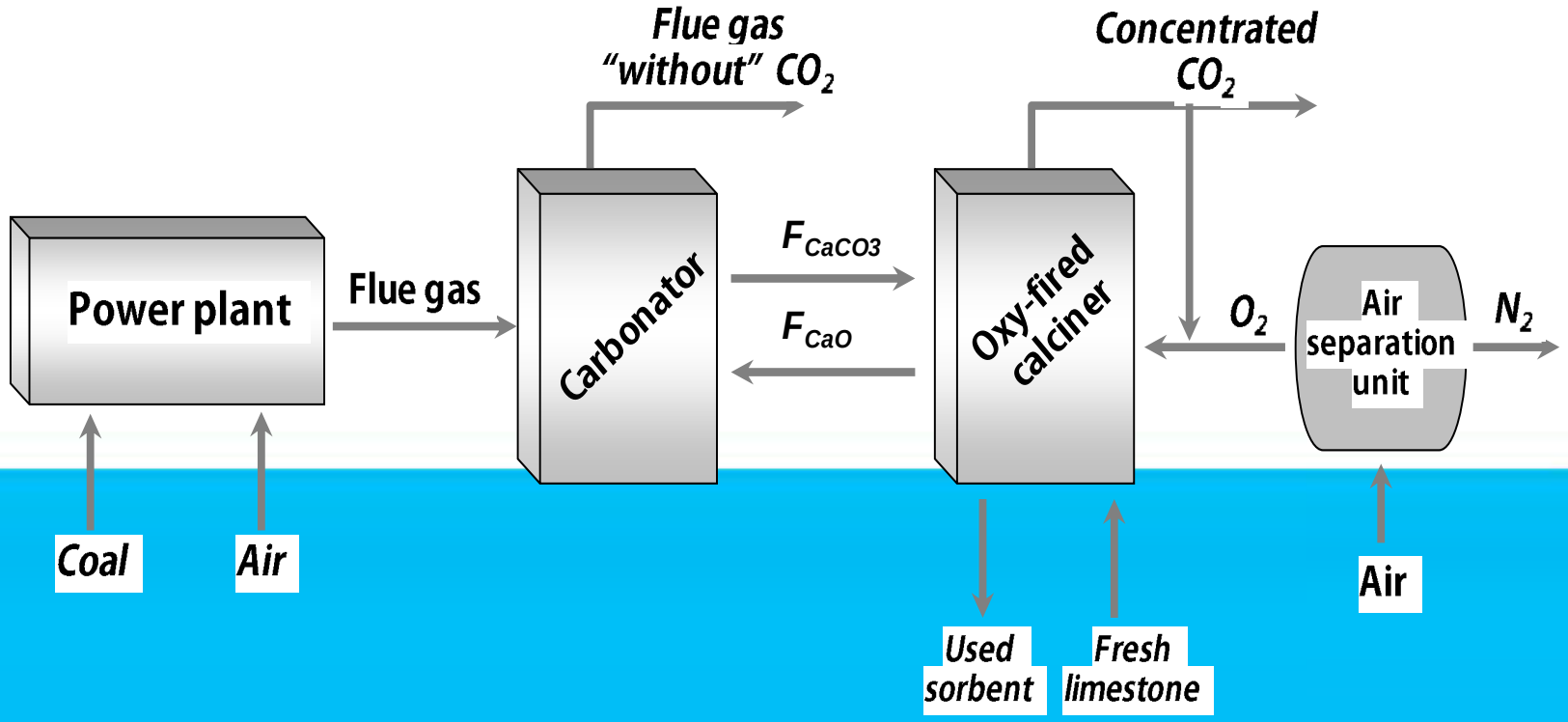
Ca and Chemical Looping

- These technologies are methods of removing CO_2 from chemical environment or bringing ‘pure’ O_2 to a chemical environment and they can be combined
- They are developed to be competitive with amine scrubbing or oxy-fuel combustion!
- The CO_2 or O_2 is transferred by particulate solid, which means that all such processes must occur at temperatures below ~1000°C
- The goal is always the production of a pure stream of CO_2 suitable for sequestration

The basic set-up for Ca Looping

$CaCO_3 = CaO + CO_2$ $\Delta H_0 = 178$ kJ/mol

$Log_{10}PCO_2$ [atm] = 7.079 - 8308/*T* [K]



Ca and Chemical Looping

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- It also means that fluidized beds must be employed, because of the scale requirements!

- Fluidized beds of sizes around 550 MW_e are now being built
- The key point of both technologies is that they look as if they can compete with amine scrubbing!

CLC and Ca Looping pilot facilities

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Organisation	Capacity & spec.	Application & features
CSIC, Spain	500 kWth; twin FB	Different coal combustion; Fe based oxygen carrier
Chalmers, Sweden	100 kWth	Mexican pet.coke; Limenite based oxygen carrier
TU Darmstadt, Germany	1 MWth – Ca and CLC	Coal gasification; limenite;
IFK Stuttgart, Germany	10 kWth; BFB &DFB	Iron based oxygen carrier
Western Kentucky Univ.	10 kW; fixed bed	Ni and Cu based oxygen carrier
Cenovus Eng. Inc. (plans to build by end of 2014)	10 MW; DFB	Ni based oxygen carrier
CaOLing (finished 2013)	1.3 MWth Ca Looping	Framework 6 Demonstration
Calix Project (finished April 2014)	3 MWe High Press Ca Loop £5.8 million	DECC Demonstration

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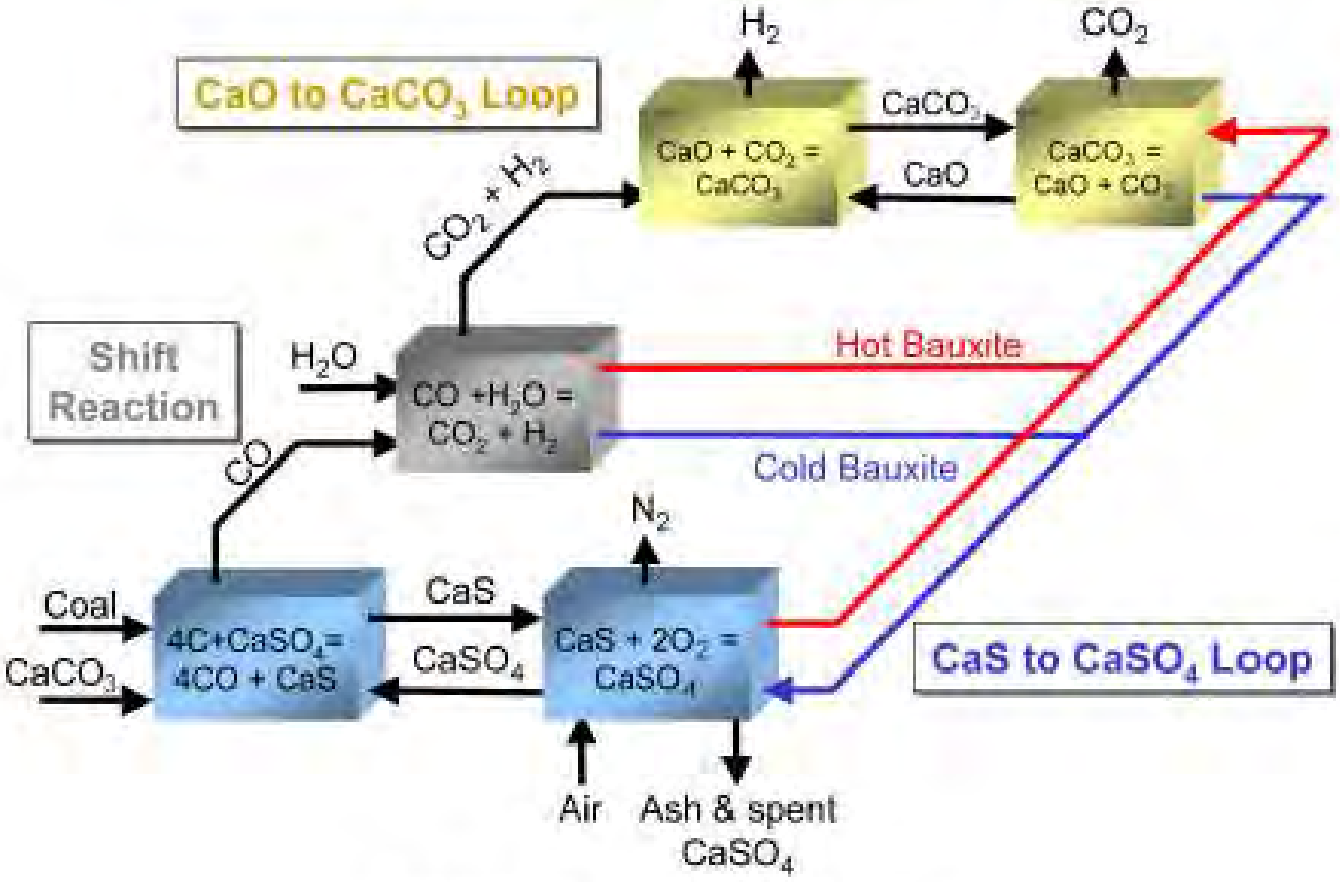
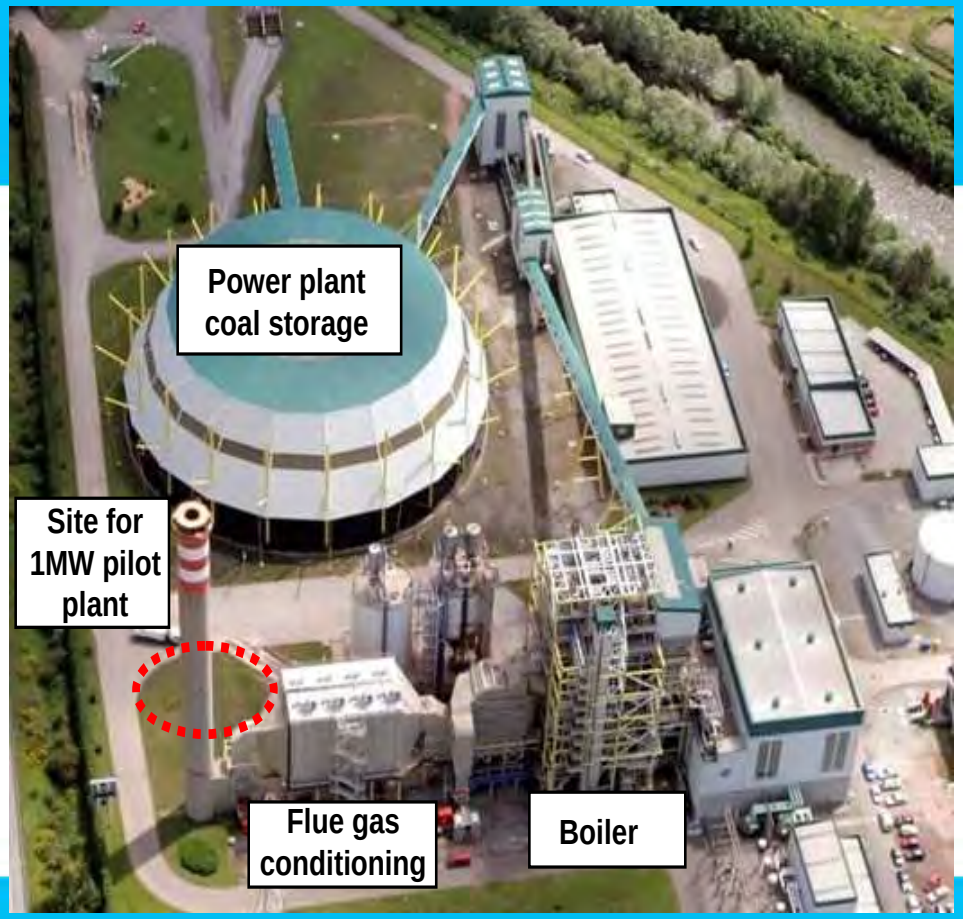
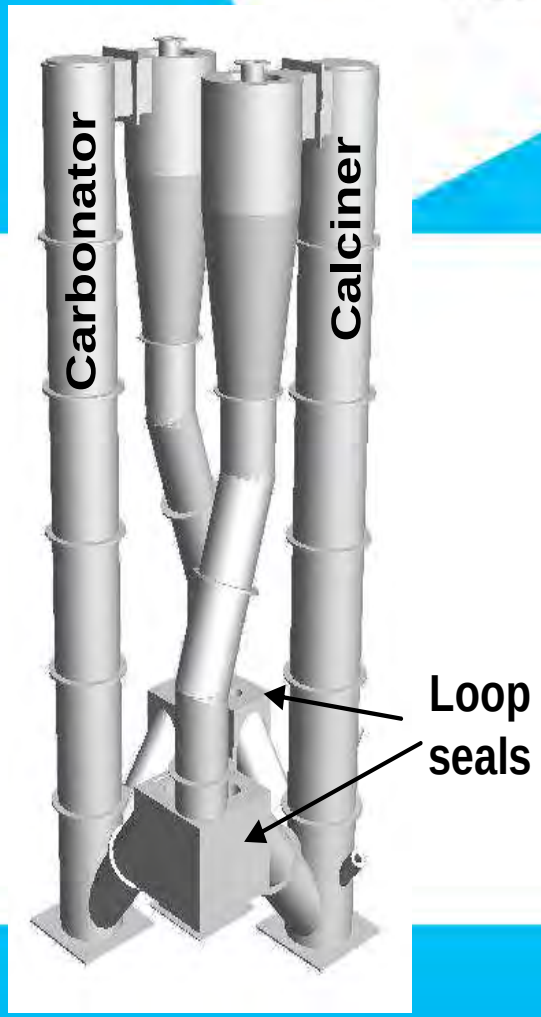
Alstom's Concept



Advanced Chemical Looping Process

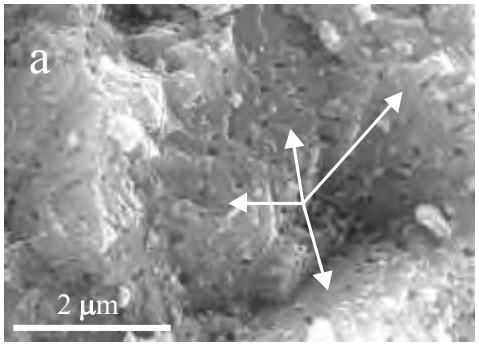




La Pereda" power plant and diagram of the carbonator and calciner reactors.

Sorbent Deactivation

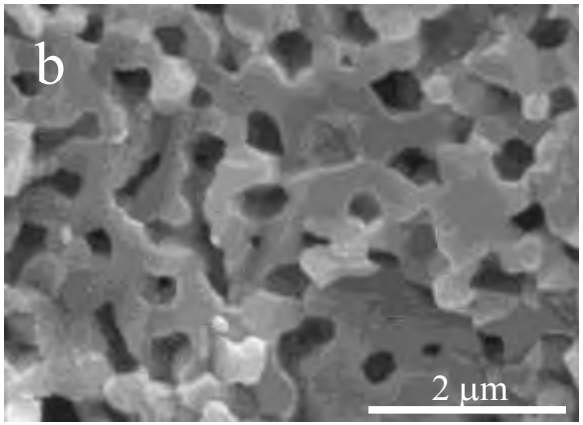
1st carbonation



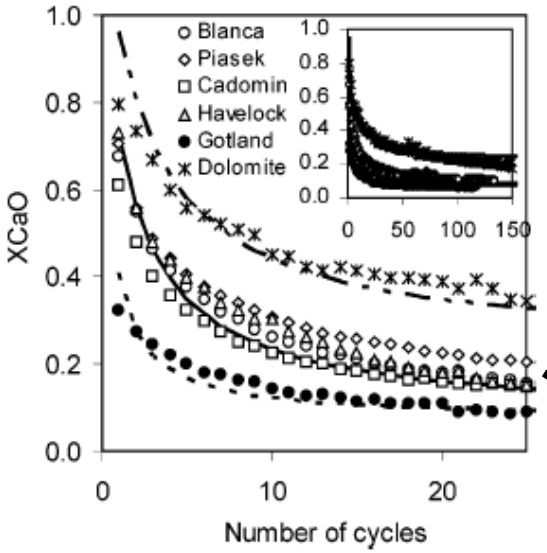
Sintering

Sorbent Decay

30th carbonation



Abanades, J., Alvarez, D., Energy & Fuels 17 (2003), 308-315



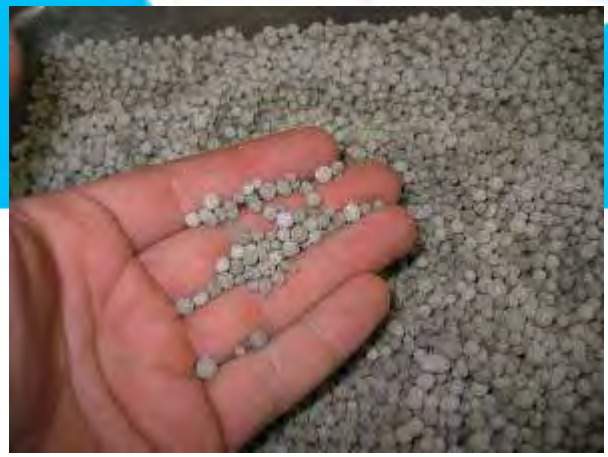
Grasa, G.S., Abanades, J.C., Ind. Eng. Chem. Res. 2006, 45, 8846-8851

During calcination ($CaCO_3 \rightarrow CaO$)

- formation of CaO, having a pseudo-lattice of calcium carbonate (rhombohedral)
- recrystallization to calcium oxide lattice (face-centred cubic)
- sintering to lower free energy lattice structure

$$X_N = \frac{1}{\frac{1}{1 - X_\infty} + kN} + X_\infty$$

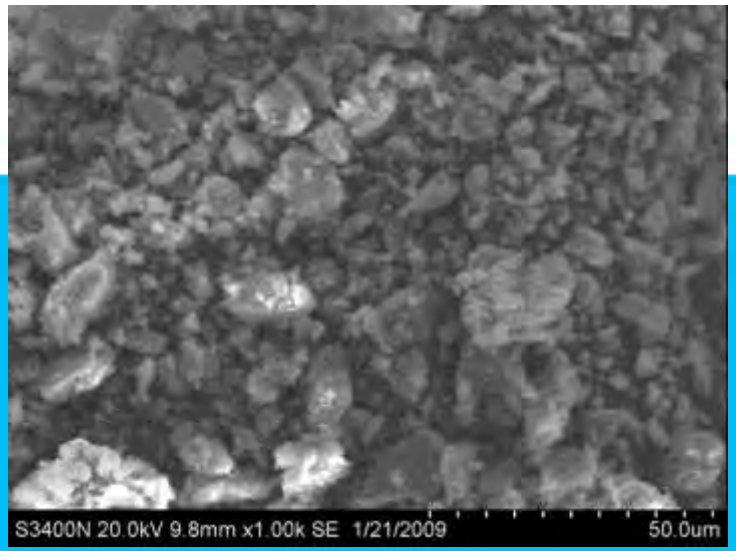
Pelletization

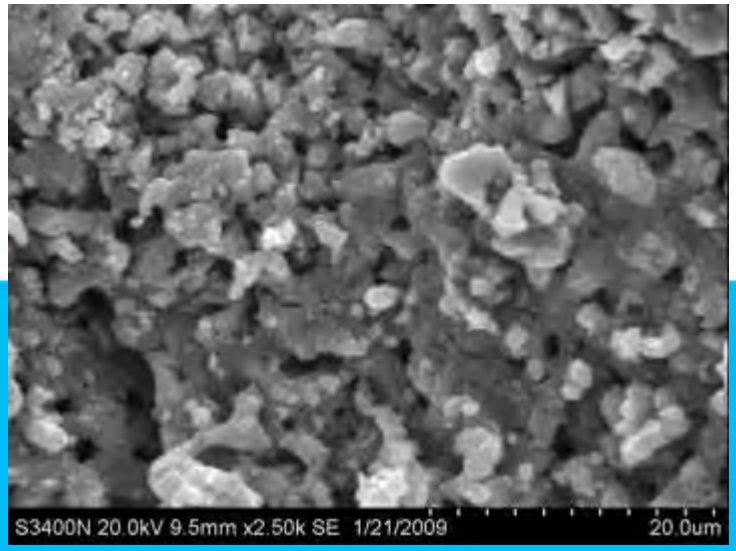


Sorbent is pulverized (<75 micron), combined with a binder, and then formed into a pellet of suitable size for FBC

Thermal treatment is necessary before injection into the FBC for conventional binders

Spent sorbent can be re-activated and reused-recycled

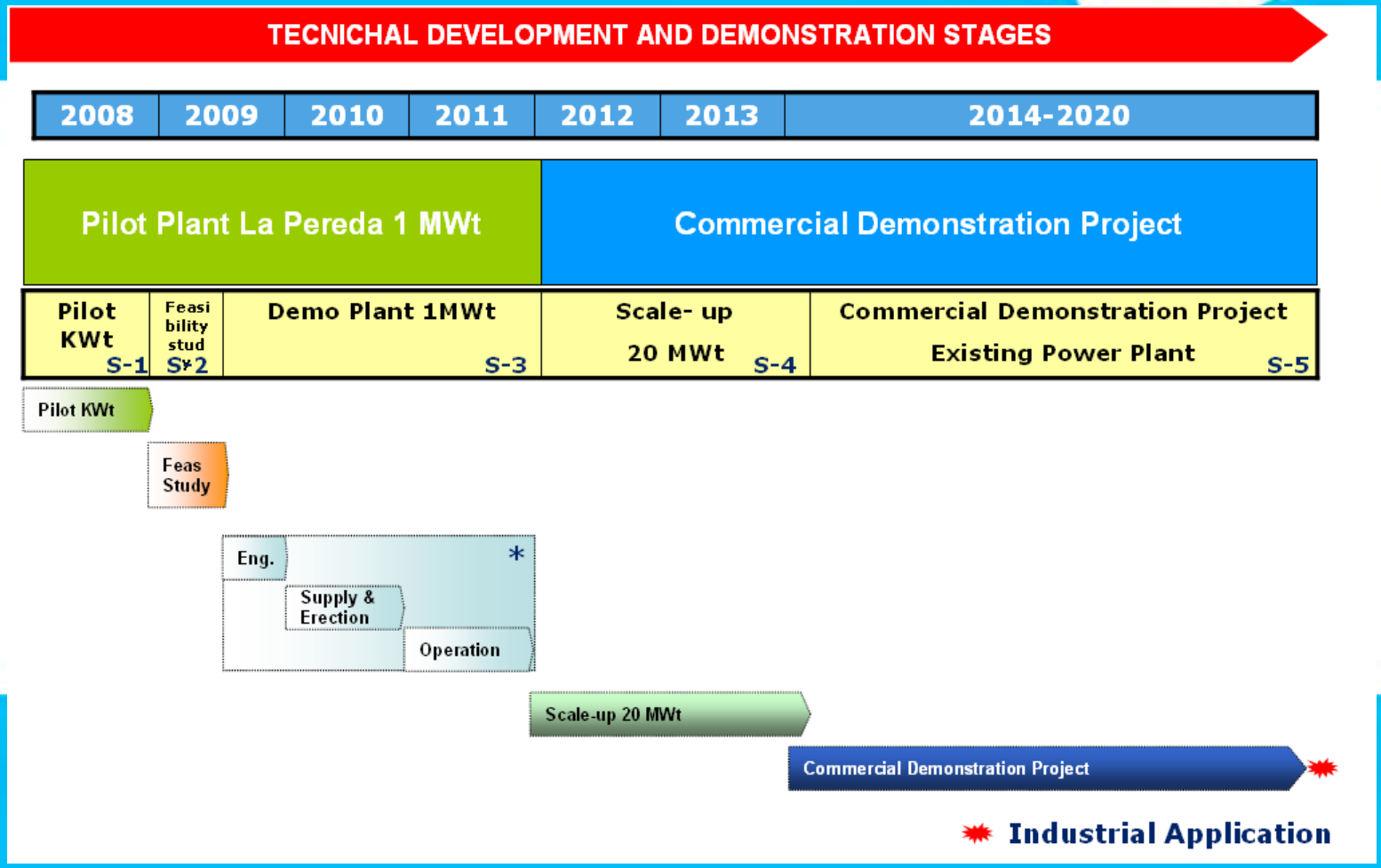




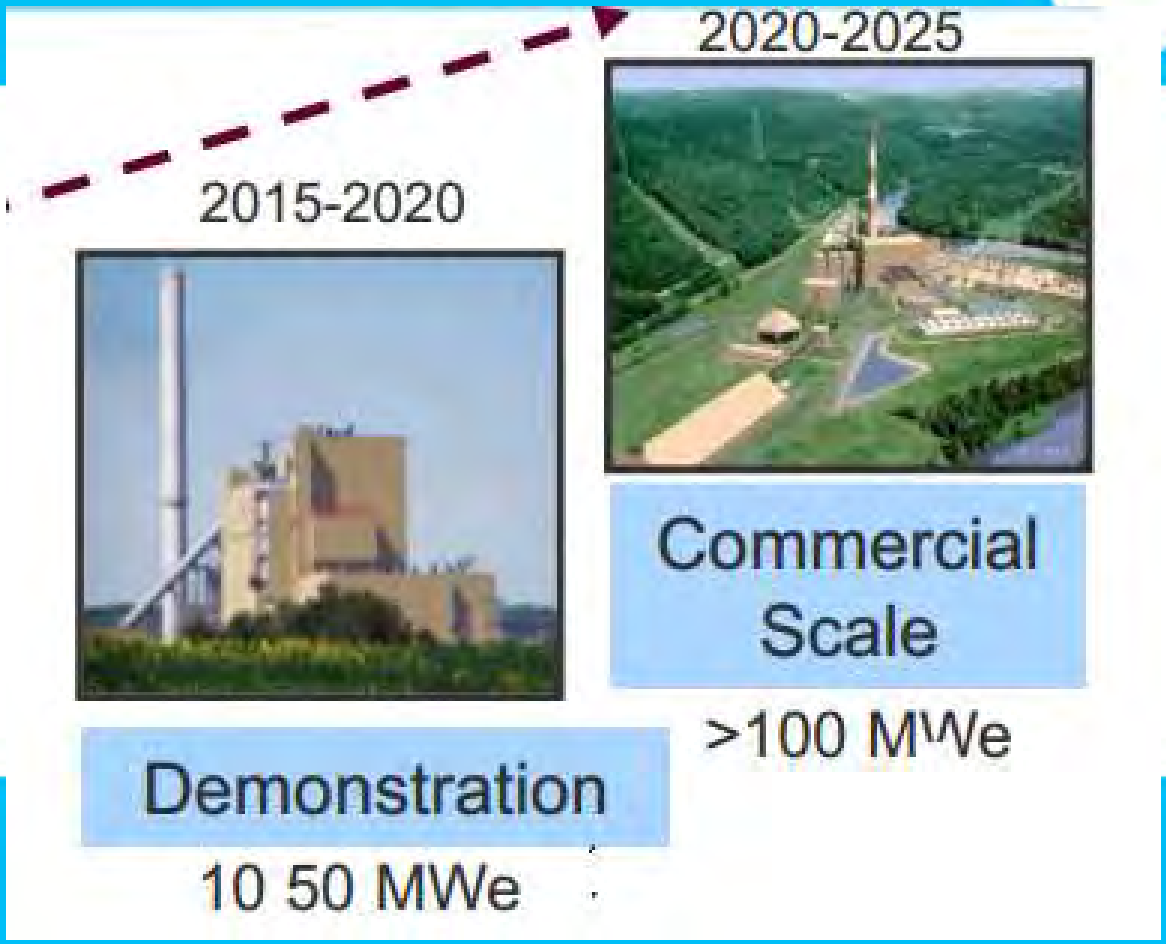
Ca Looping – State of the Art

- CO_2 capture efficiencies 90% achievable in a CFB carbonator reactor operating with “standard” solids, bed inventories, gas velocities and solid circulation rates.
- SO_2 capture in the CFB carbonator is over 95%.
- Initial results indicates that sorbent activity decay penalty less than expected.
- The concept of post-combustion Ca-looping in continuous mode of operation has been successfully proven with two interconnected CFBCs at the MWth scale.

CaOling Roadmap

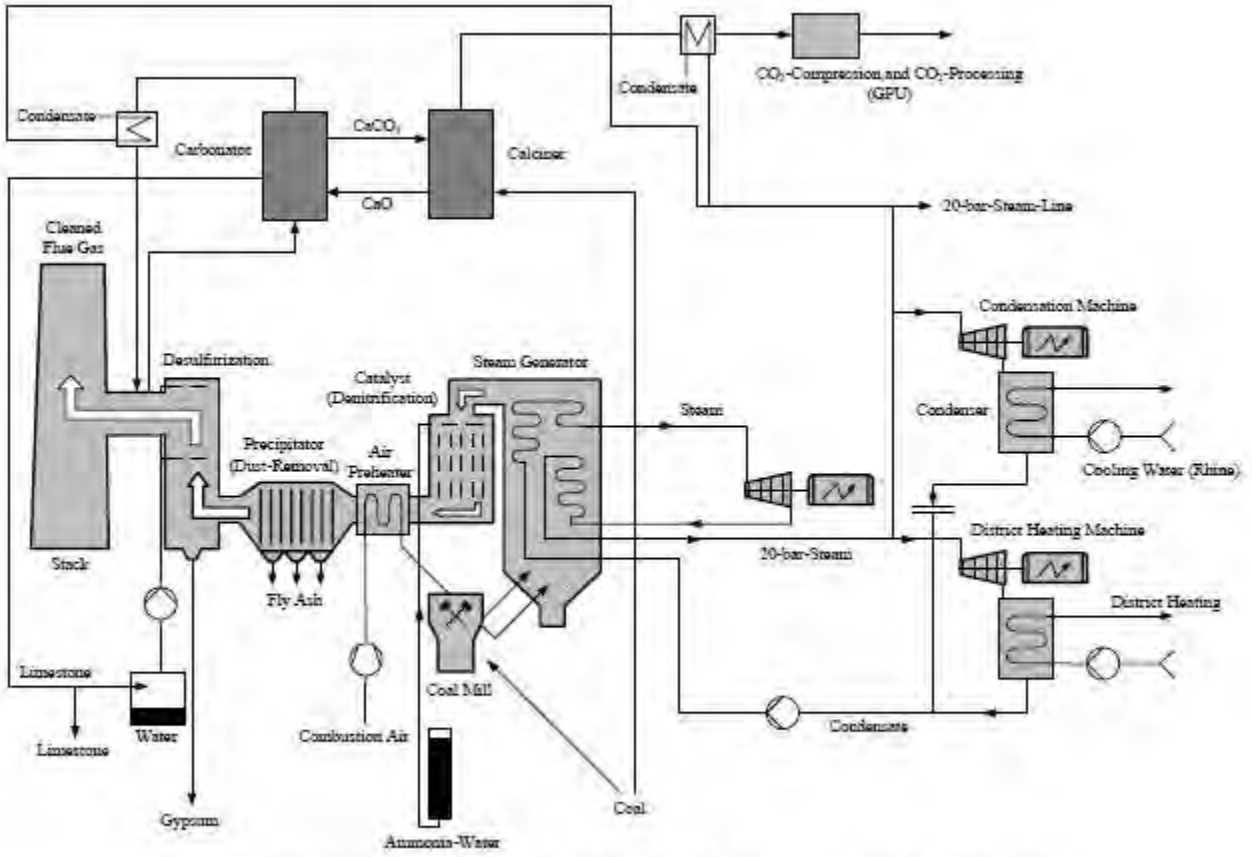


The Alstom Vision



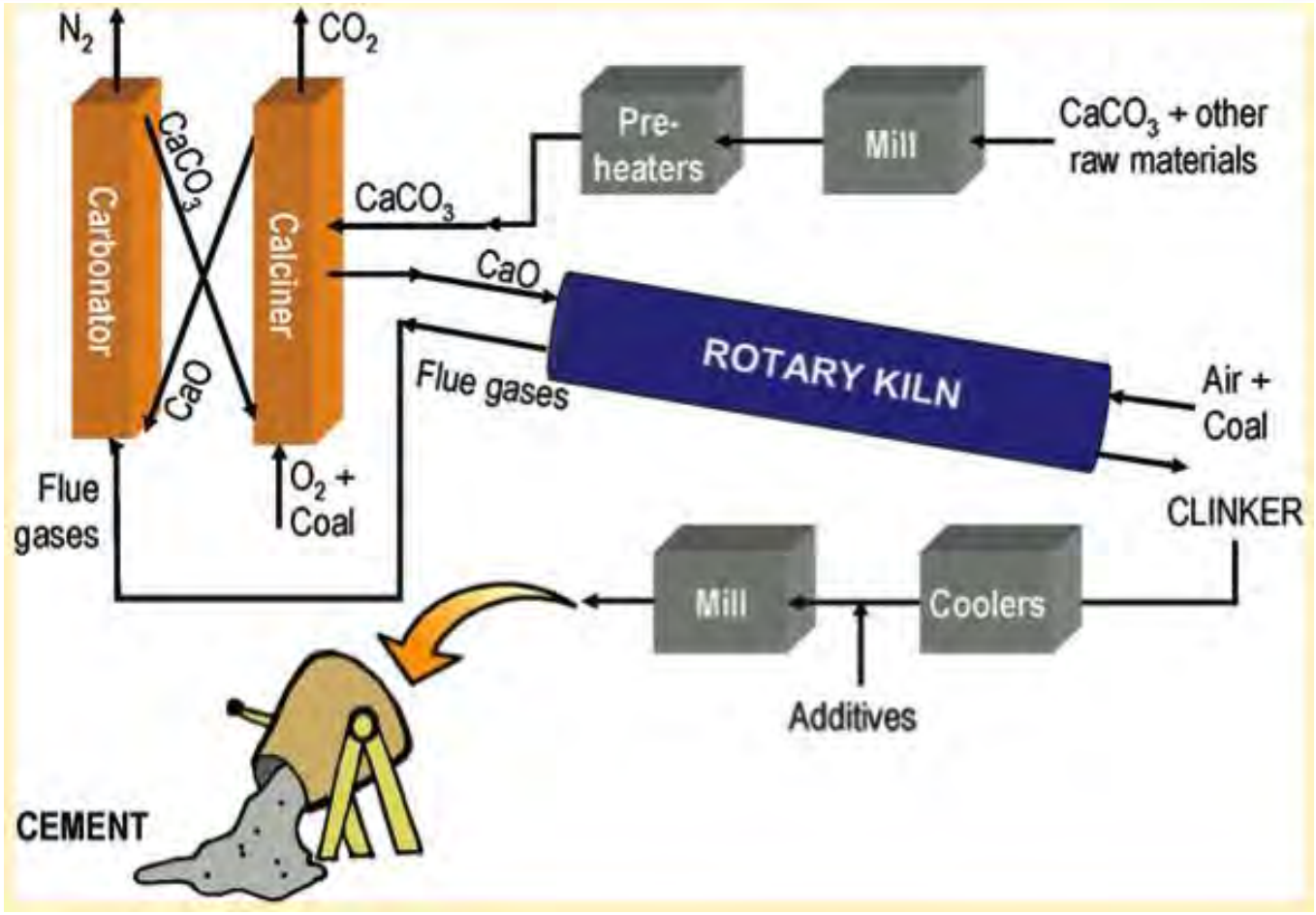
http://www.netl.doe.gov/file%20library/research/coal/carbon%20capture/abdullally-alstom-clc-prototype.pdf

The Standard Bearer for Ca Looping – University of Darmstadt



Integration of the 20 MW_{th} pilot into the GKM power plant site

Ca Looping with Cement Manufacture



Global Production of CaO from CaO Looping assuming the technology was used for all Coal Fired Plant together with data on cement production

Region	Coal-fired Electricity Generation 2009 (TWh)	Proposed Coal Fired Plant Capacity (GW) [1 GW →0.9 TWh/y max.]	Maximum Lime Production from Ca Looping on Current Coal-fired Power Generation (Mt/y)	Maximum Cement Production from Ca Looping on Current Coal-fired Power Generation (Mt/y)	Cement Production 2012 (Mt/y)
UK	105	-	9	14	8.5
US	1890	20	166	256	74.9
China	2892	558	254	391	2,210
India	615	519	54	83	270

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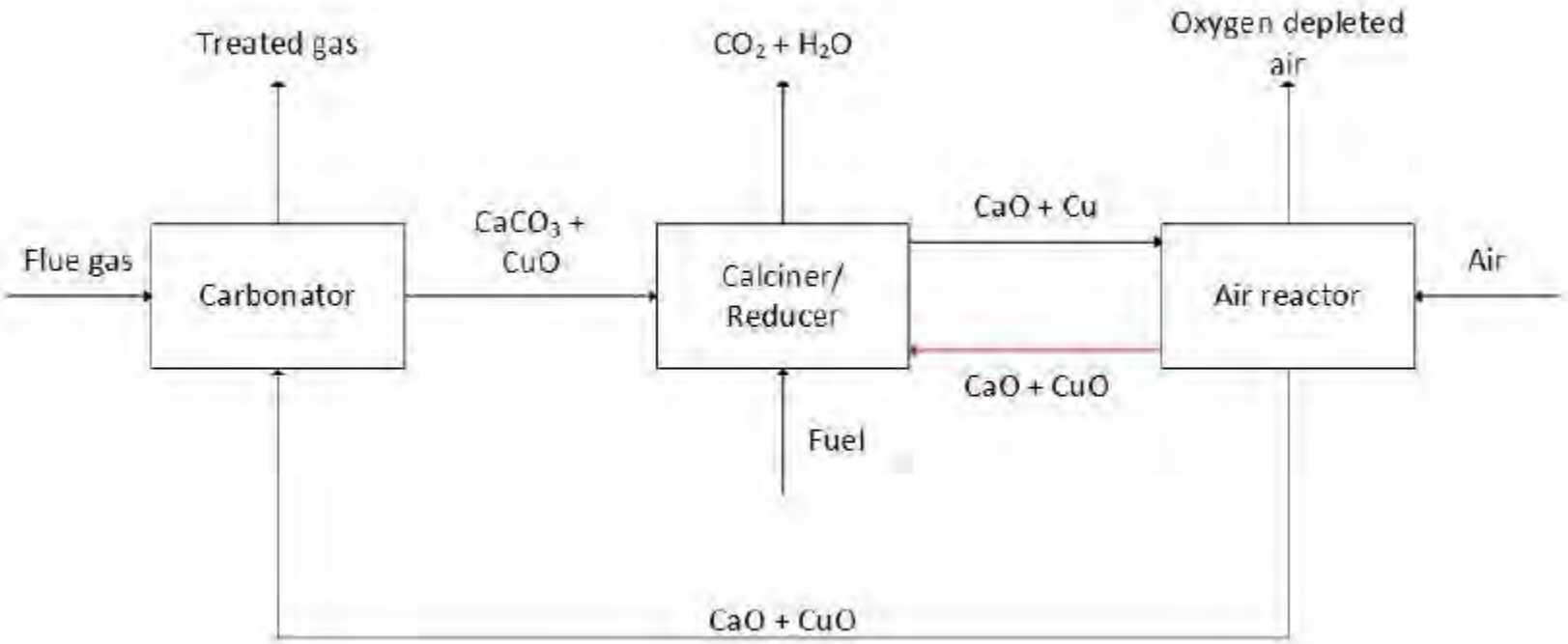
Table 11: Simulation assumptions summary - Modified CaL-CLC processes.

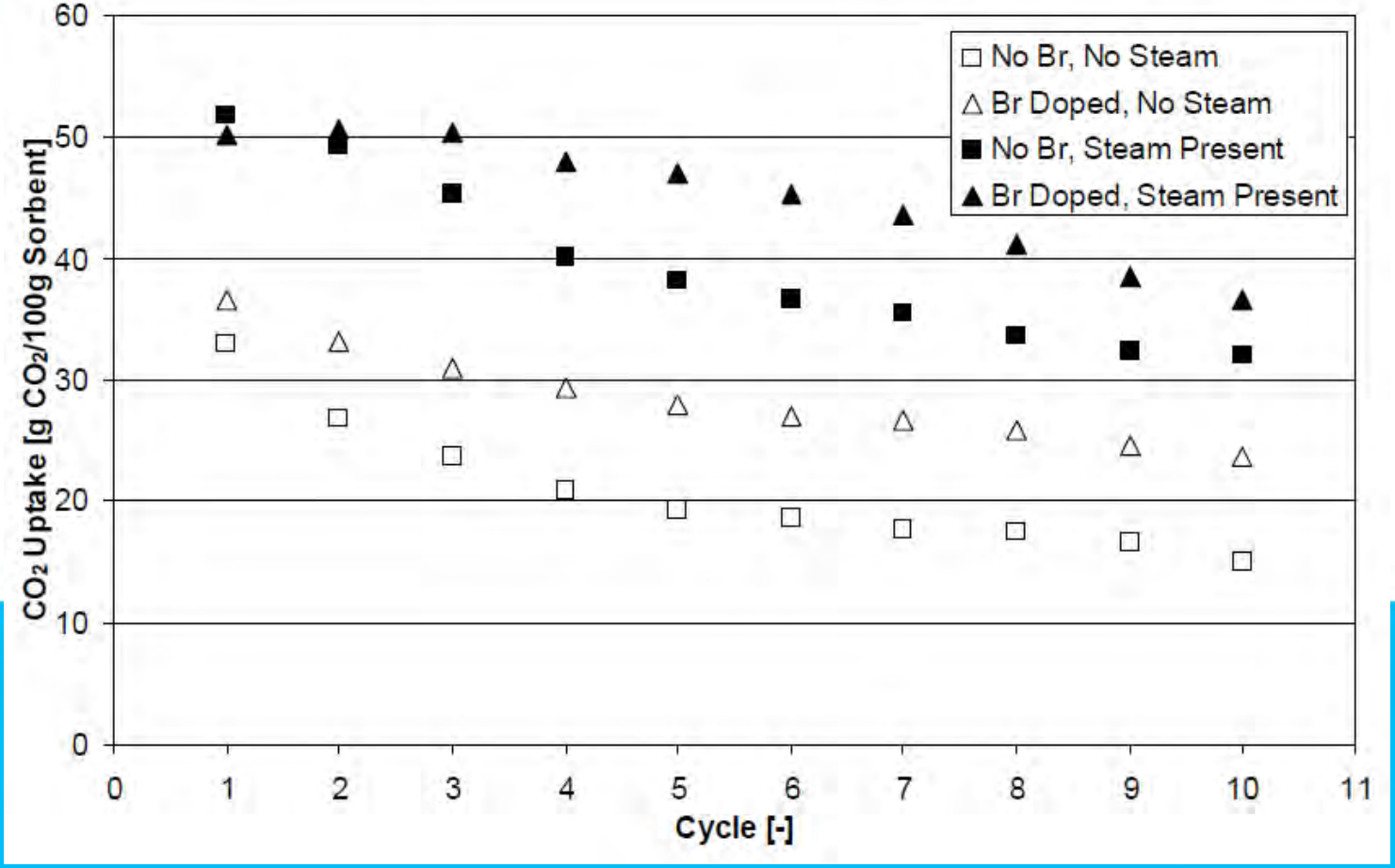
Reactors simulation	Ca activity	Cu activity	Flue gas
Gibbs reactor are used for all reactors	Ca activity = 15%	100%	350°C – 1 atm
Copper excess	**Carbonator operating conditions**	**Calciner operating conditions**	**Air reactor operating conditions**
20%	650°C – 1 atm	920°C – 1 atm Complete calcination Complete reduction	970°C – 1 atm Complete oxidation 5% excess air
ASU energy consumption	**CO_2 purification and compression**	**CaL loop - Pellets support**	**CLC loop – Pellets support**
200 kWh/t O_2	110 kWh/t CO_2	10 wt% Al_2O_3	50 wt% Al_2O_3
Fuel	**Gas-solids separation**	CaL/CLC solids separation	
Pure methane	100% efficiency	100% efficiency	

Combining Ca and CLC

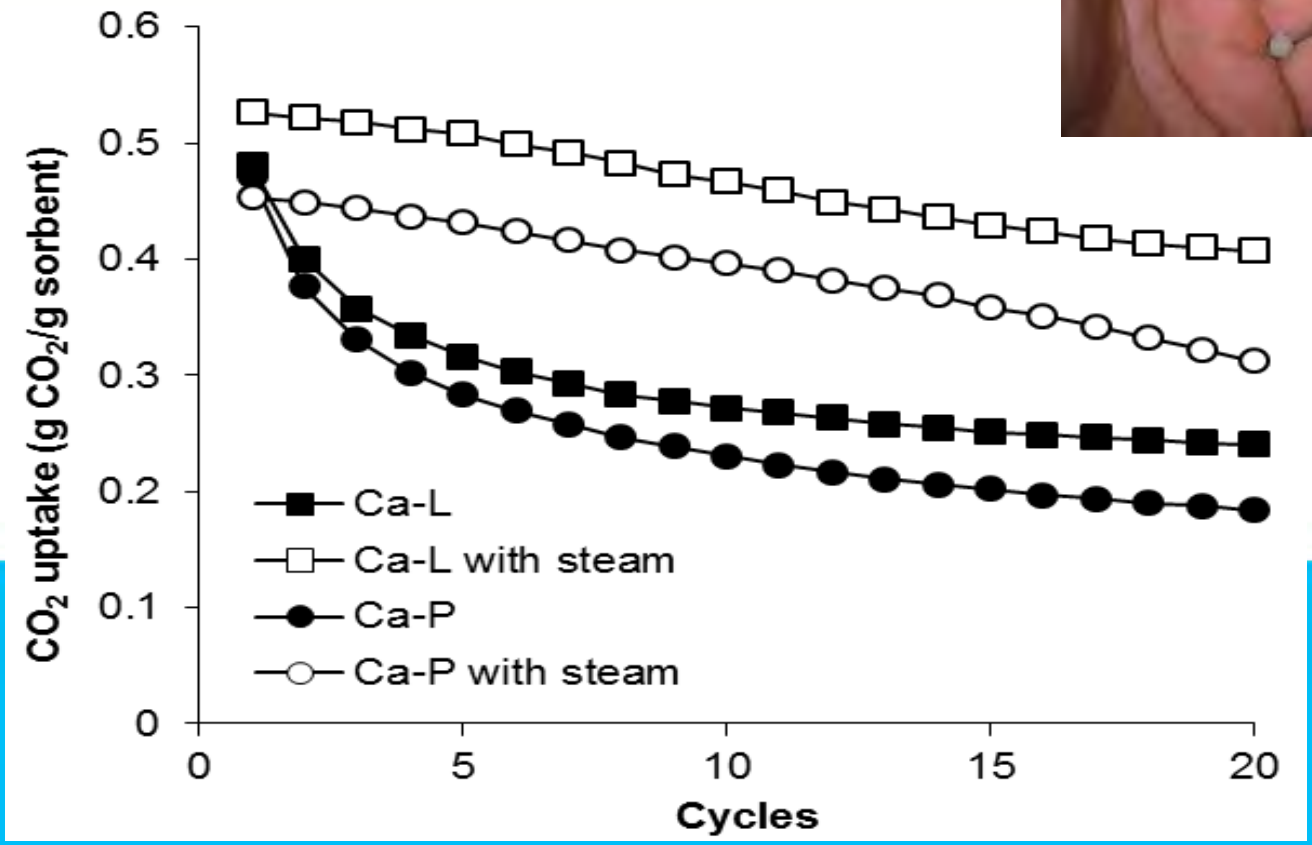


Overall net power output (MWe)	715.45	1783.02	1156.99
Overall net efficiency (HHV)	29.73%	31.94%	31.70%
Energy penalty (%)	23.74%	18.07%	18.67%

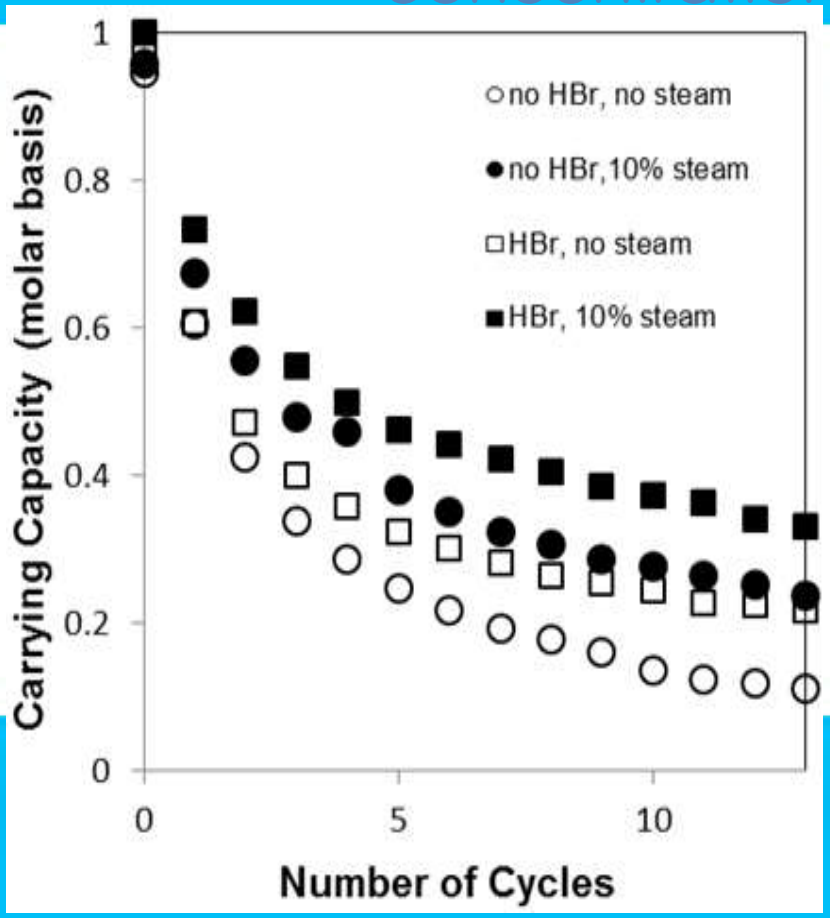
Additives to improve Ca Looping Sorbents



Templating Sorbents



Additive effects between most effective HBr dopant concentrations and 10% steam

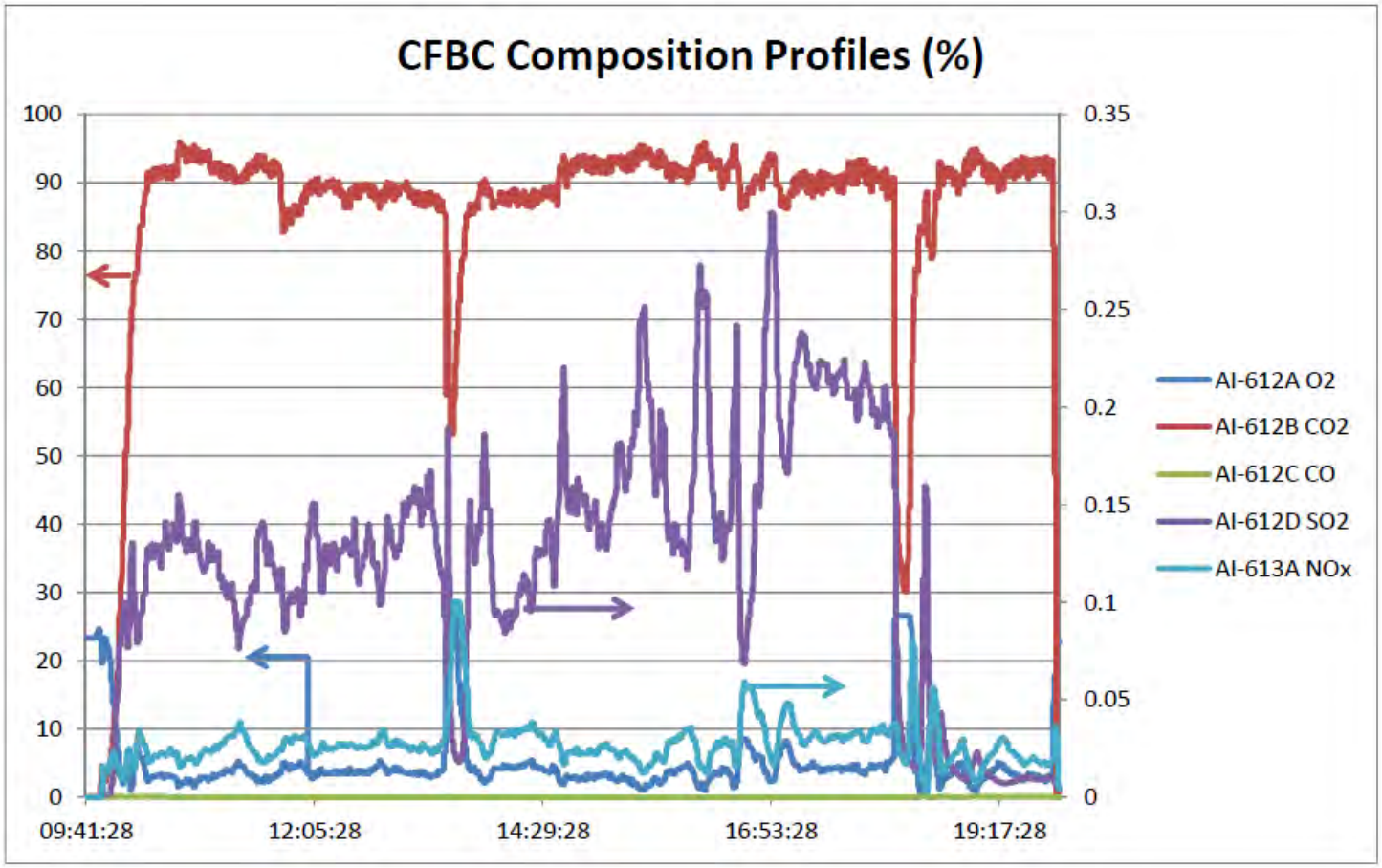


Carrying capacities are in mol/mol of the calcined material

The combined presence of steam and dopant significantly increased the carrying capacity of the sorbent

Carrying capacity of Longcliffe limestone over 13 cycles with and without steam and with and without dopant:

High O_2 Concentrations in a 50 kWth CFB – 35% O_2



CaL modelling activities

To investigate the integration opportunities, the following models have been built in Aspen Plus® allowing for a process-wide analysis:

- 580 MW_{el} (base-load) and 660 MW_{el} (part-load) supercritical coal-fired power plants.
- Calcium looping CO_2 capture plant.
- CO_2 compression unit and cryogenic air separation unit.

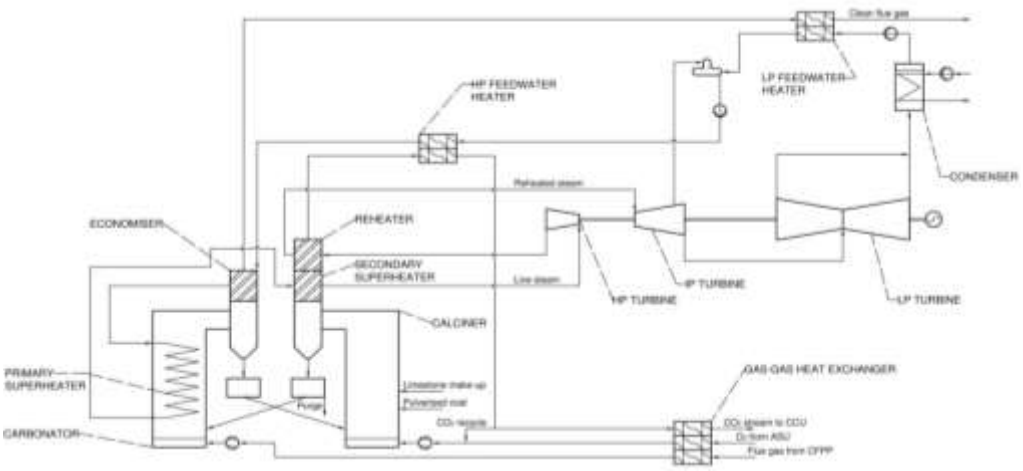


Figure 1: CaL integrated with secondary steam cycle

Preliminary integration study revealed that the efficiency penalty is 7 – 8% points.

Current modelling activities include:

- Parametric and multi-variable optimisation.
- Heat exchanger network analysis.
- 3-E (Energy, exergy, economic) analysis.
- Advanced integration scenarios.
- Alternative process configurations.

Hanak D. P., Manovic, V., and Anthony E. J. (2014), "The Future of Ca Looping - A review of developments", IFSA 2014 Industrial Fluidization South Africa, pp. 9-33.

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Conclusions

- Both Ca and CLC have reached the “large” pilot scale level, and both have been shown to be functional technologies offering cheaper CO_2 separation
- However, the next stage, full-scale demonstrations are now frozen due to inadequate government funding everywhere!
- In the meantime R&D is continuing a pace in various centres to improve (and even combine) the two technologies but most developments are incremental!
- More innovative strategies incorporating the technology with cement manufacture or using high O_2 levels in the calciner are and need to be explored

Acknowledgements

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