The Integration of Power Generation, Cement Manufacture, Biomass Utilisation and Calcium Looping.

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Imperial College London, February 2013.

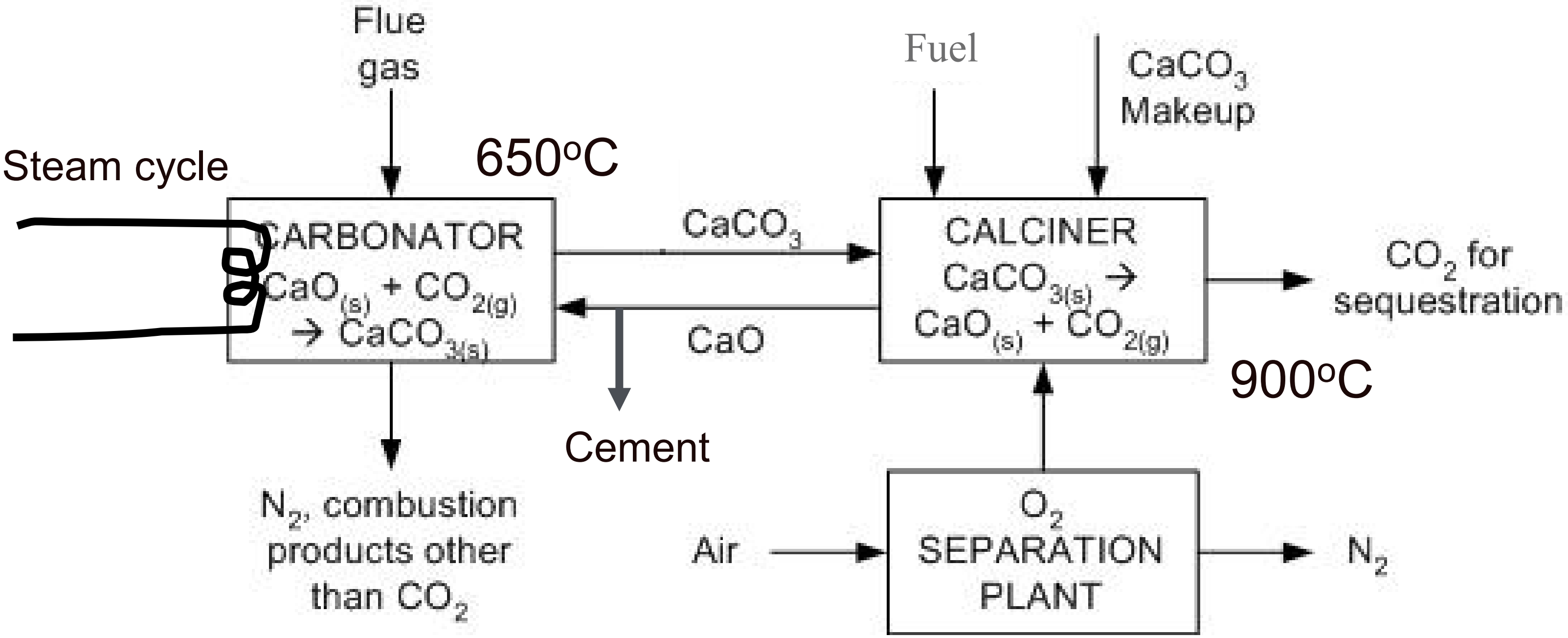
Funded by EPSRC and Cemex UK Ltd.

Outline of presentation

- Flowsheeting – integration of power generation, calcium looping, biomass utilisation and ocean liming.

- Experimental work – integration of power production, calcium looping, biomass utilisation and cement manufacture.

Example Scheme for Post Combustion CO_2 Capture with Ca Looping

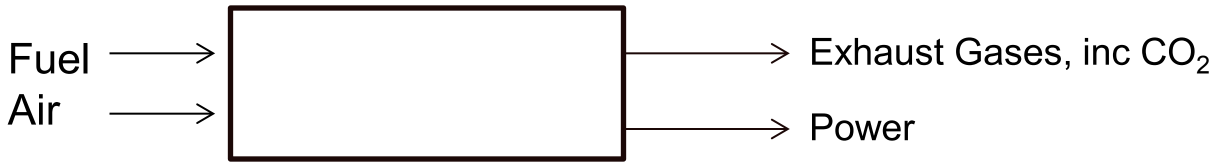


- A simple flow diagram for a post combustion carbon capture process harnessing calcium looping is shown
- The sorbent is continually cycled between the carbonator and calciner and acts as a CO_2 carrier, taking CO_2 from a stream of gas of a relatively low $ppCO_2$ in the carbonator, providing a stream of a high $ppCO_2$ in the calciner
- Potential efficiency penalty of only 5 %, *excluding* savings from integration with cement industry – key is the heat recovery in the carbonator

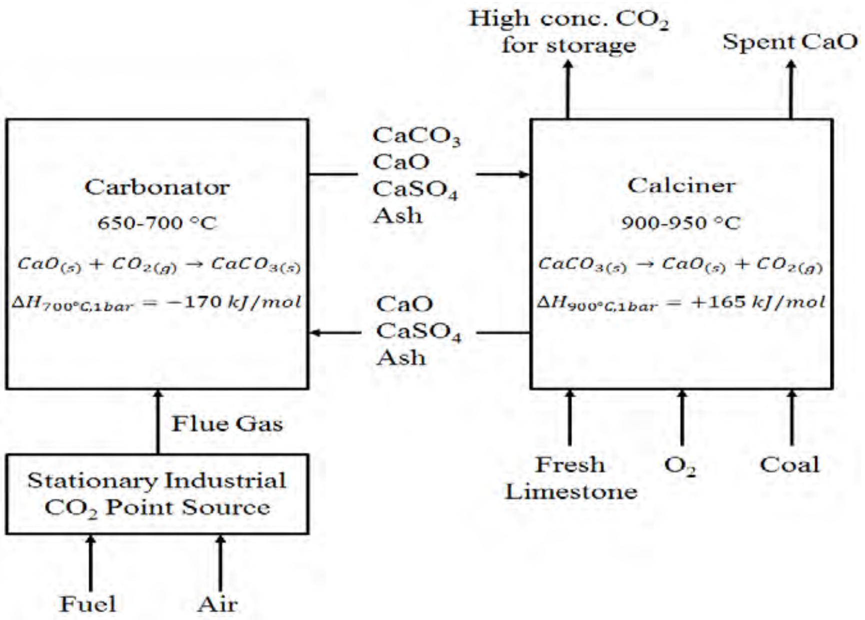
Technoeconomic study

- Similar to Tesbic, but done independently
- Aim – to determine which of:
  - Biomass
  - Ocean Liming
  - CCS
- Contributed most to reducing the avoided cost of CO_2
- Initial study – rough and can most certainly be improved

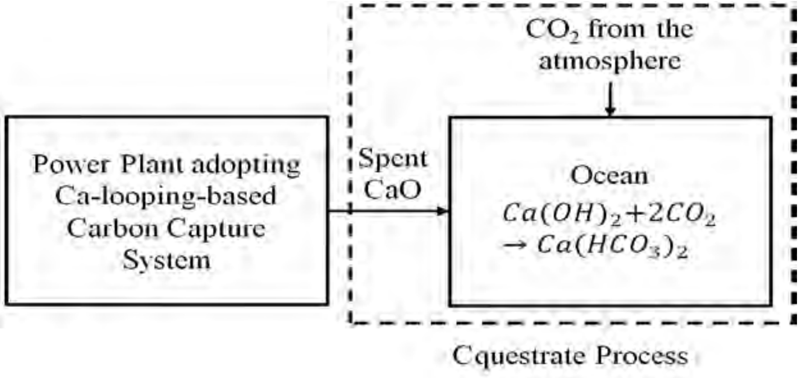
Biomass + Ca looping + Ocean Liming



Combustion



Post-Combustion Ca looping



Integration with ocean liming (Cquestrate)

Integrated Model(s) of all technologies

Key Features and Assumptions of Model

- Flowsheet implemented in Aspen Plus
- Separate blocks for Calciner, Carbonator, ASU, Turbines and CO_2 compression
- Key assumptions – 95 % CO_2 capture (a little high, but does not affect overall results too much)
- Refrigeration COP in ASU 3
- Basic steam cycle efficiency 42.1 % for coal power plant (both heat and turbine systems require further optimisation)
- CAPEX 25 % higher for biomass systems
- Biomass cost $70 / ton: Coal cost $110 / ton. LHVs 16.2 and 27.3 MJ/kg.
- CO_2 compressed to 74 bar
- Pumping costs included where necessary
- Retrofit reduces efficiency (heat integration poor)

All cases individually optimised

Key Assumptions - economics

- All costs rebased to $\$_{2011}$ using capital cost escalation curve[1]
- Power island and boiler costs from GCCI[2]
- Ancillary costs from McKenzie et al 2007[3]
- Availability between 90 % (PF Coal) and 75 % (Biomass + CCS + ocean liming).
- Individual units sized and costed
- Other Assumptions

Raw materials (Limestone)	= 25 $/tonne
Raw material transportation	= 10% of RM
Labour/Overheads	= 10% of Variable
Utility Requirements	= 15% of Variable
Maintenace & Repairs	= 5% of fixed capital
Supplies	= 15% of maintenance

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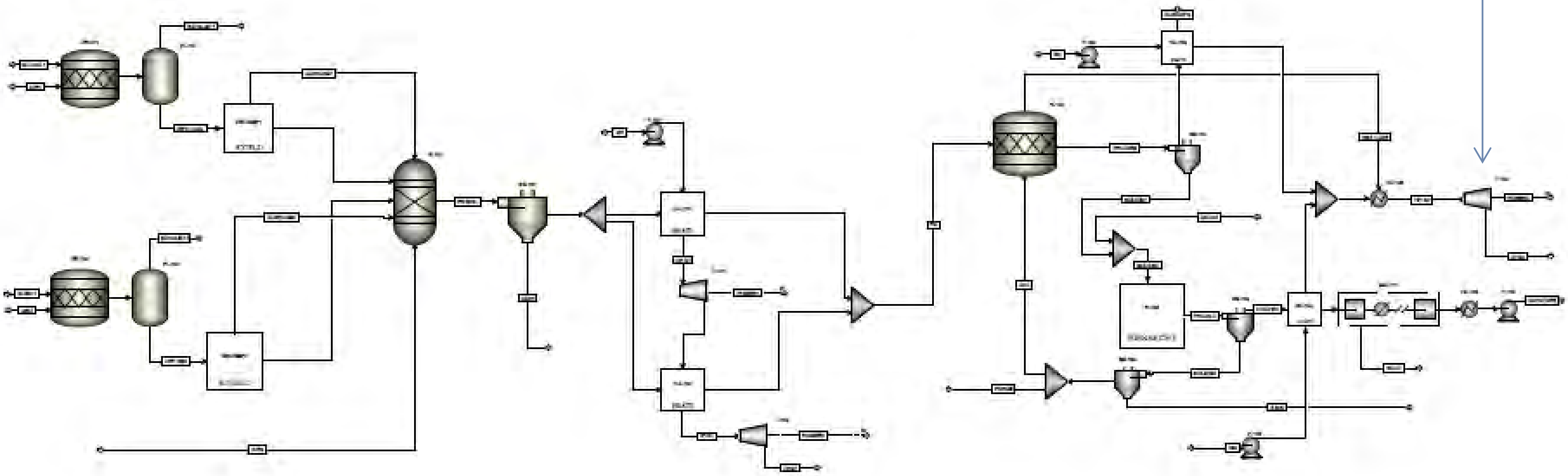
[1] IHS, 2011, IHS Indexes, Available at: http://www.ihsindexes.com/, last accessed: 24/04/11.

[2] Global CCS Institute Strategic Analysis of the Global Status of Carbon Capture and Storage Report 2: Economic Assessment of Carbon Captureand Storage Technologies)

[3] MacKenzie, A., Granatstein, D.L., Anthony, E.J., and Abanades, J.C., Economics of CO2 Capture Using the Calcium Cycle with a Pressurized Fluidized Bed Combustor. *Energy & Fuels*, 2007. **21**: p. 920-926.

Basic Aspen Model



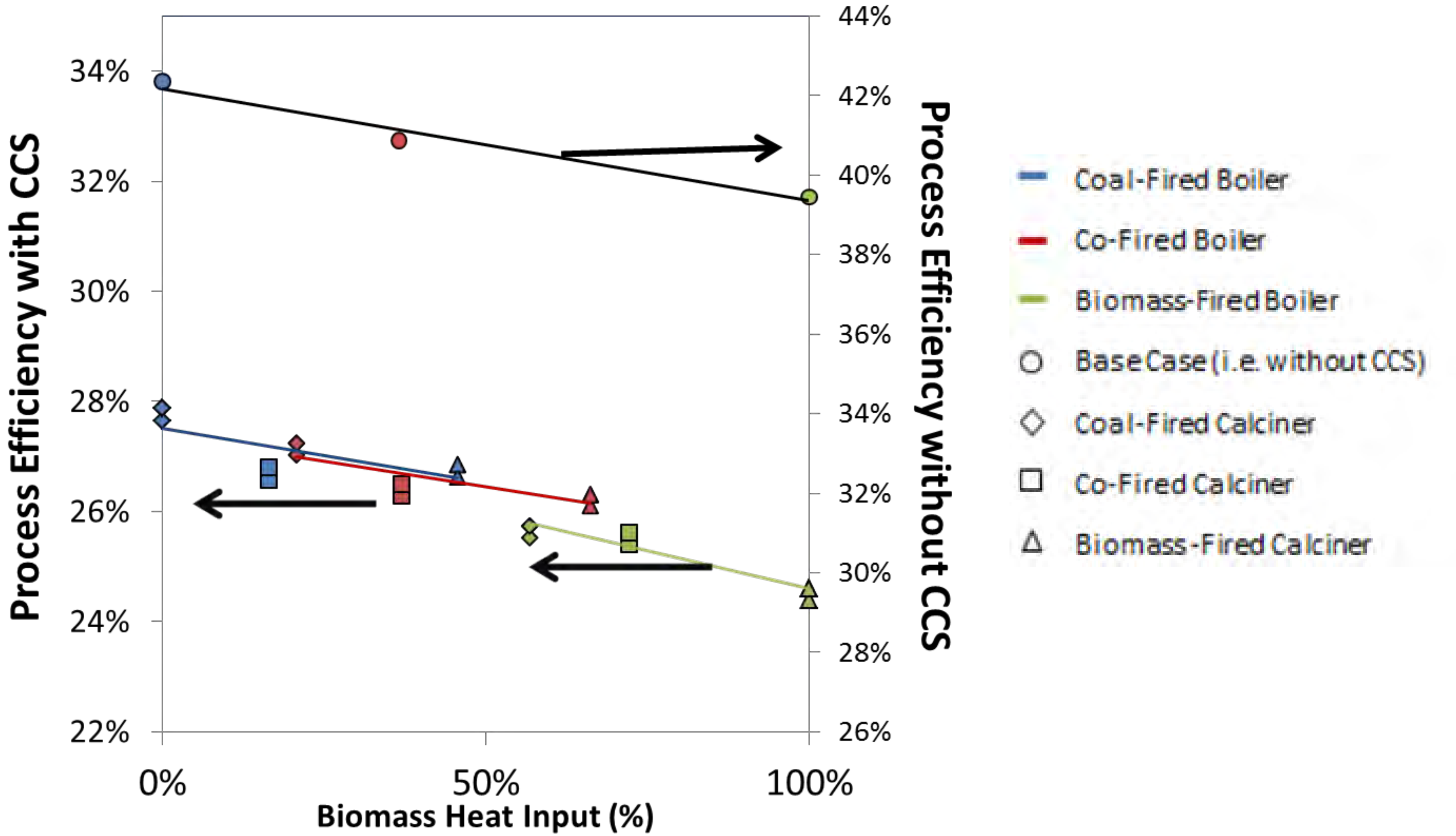
New Turbine

Drying and
Combustion
(PF)

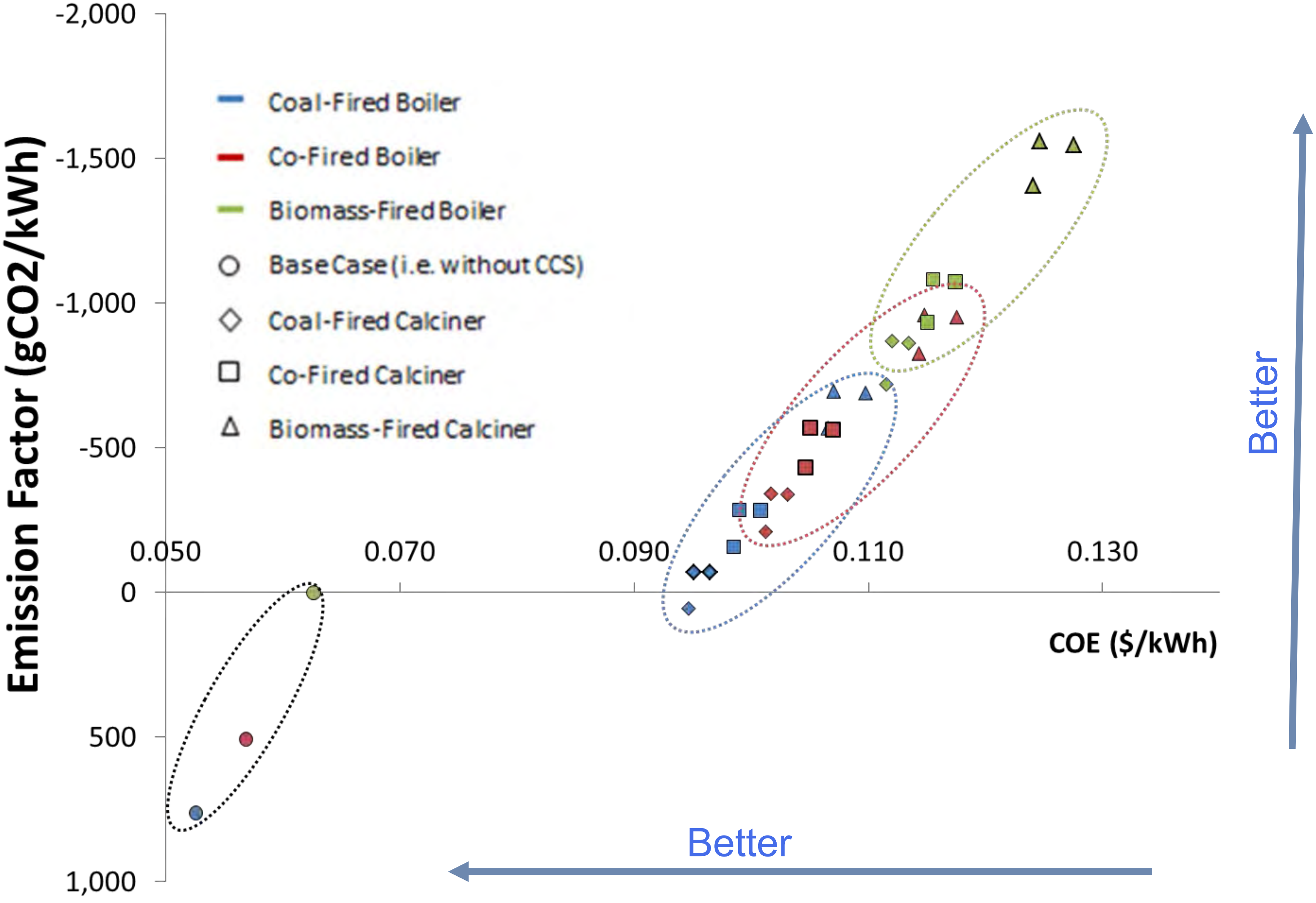
Two stage steam turbine

Ca Looping

Process Efficiency



Emission Factor and Cost of Electricity



Selected Results

Combustion Configuration	Calcium Looping (Y/N)	Calciner Configuration	Cquestrate (Y/N)	Cquestrate Type	Emission Factor (gCO2/kWh)	Process Efficiency (%)	COE ($/kWh)	AC ($/tco2)
Coal (100%)	N				762	42.4%	0.053	
Coal & Biomass (50:50)	N				507	40.9%	0.057	15.1
Biomass (100%)	N				0	39.4%	0.063	12.6
Coal (100%)	Y	Coal (100%)	N		55	27.9%	0.095	59.5
Coal (100%)	Y	Biomass (100%)	N		-569	26.9%	0.107	40.6
Biomass (100%)	Y	Coal (100%)	N		-719	25.7%	0.112	33.0
Biomass (100%)	Y	Biomass (100%)	N		-1,404	24.6%	0.124	28.4
Coal (100%)	Y	Coal (100%)	Y	On-site	-71	27.6%	0.095	51.1
Coal (100%)	Y	Biomass (100%)	Y	On-site	-696	26.6%	0.107	37.3
Biomass (100%)	Y	Coal (100%)	Y	On-site	-869	25.5%	0.112	30.3
Biomass (100%)	Y	Biomass (100%)	Y	On-site	-1,558	24.4%	0.125	26.7
Biomass (100%)	Y	Biomass (100%)	Y	Remote	-1,545	24.6%	0.129	28.9

Cheaper to mitigate CO_2 using biomass than by CCS (supply limited).

The more biomass used, the lower the avoided cost (limited by technical issues for co-firing).

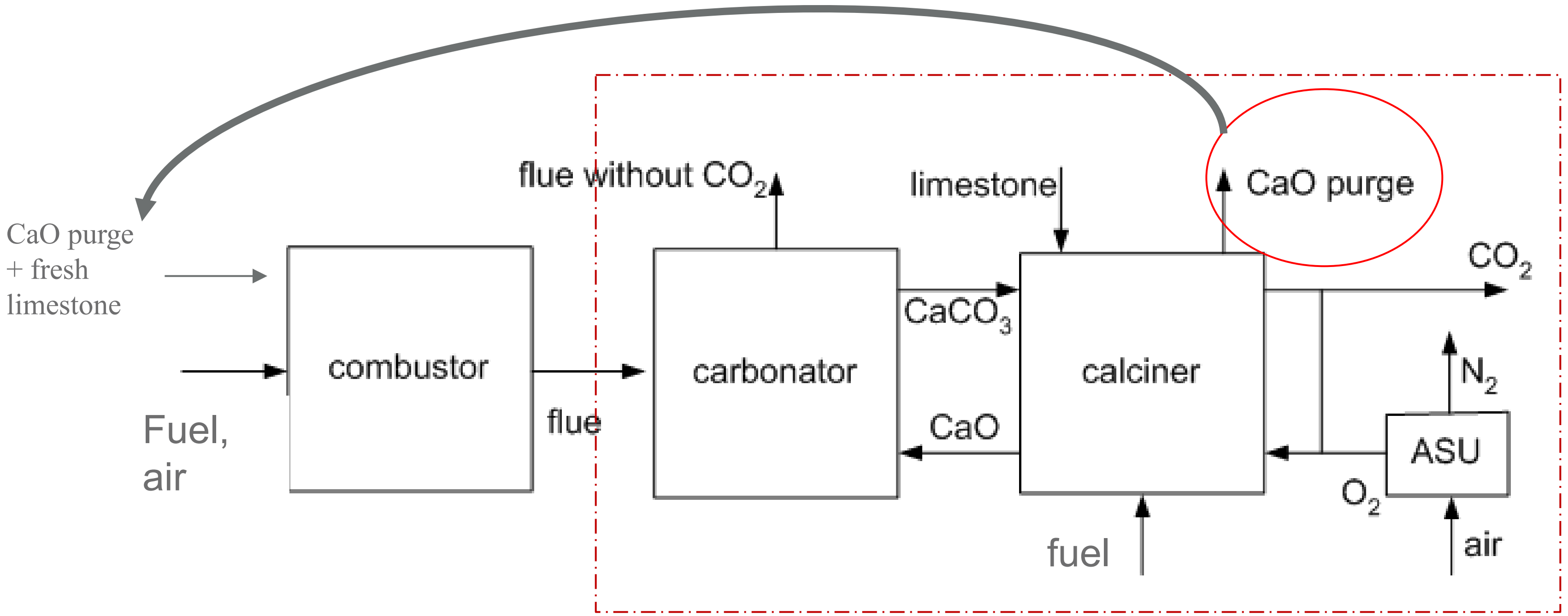
CCS efficiency penalty a little high (12 %) – better heat integration required.

On-site Cquestrate reduces costs further (~ \$2 / tCO_2 in the biomass / biomass case, ~ \$8 in the coal / coal case).

Integration with Cement Manufacture

- Short-term alternative to ocean liming
- Less potential for negative emissions
- Greater intrinsic value for spent sorbent
- Decarbonise cement manufacture by 60 – 70 % for “free”.

Post-combustion capture with Ca-looping



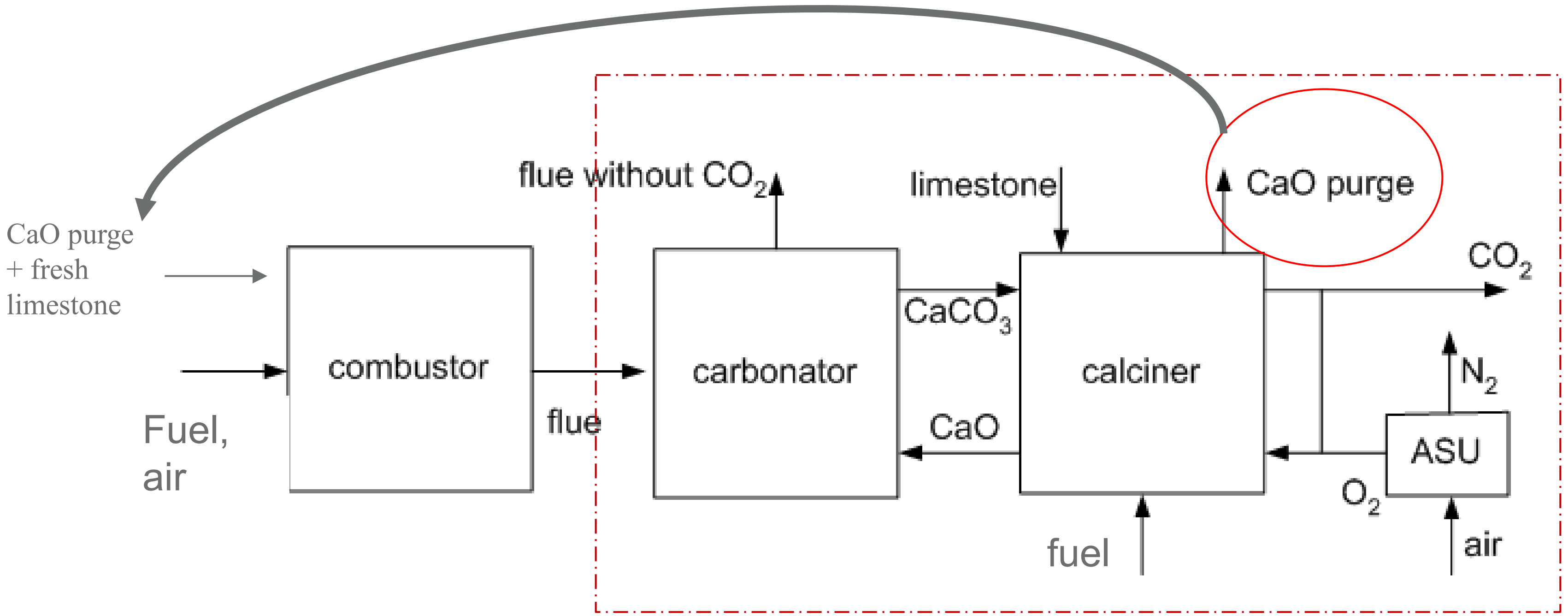
Advantages:

- limestone cheap and non-toxic
- mature CFB technology
- low energy penalty; 6 – 8 % points, inc. compression
- synergy with cement, decarbonising both processes
- simultaneous SO_2 removal

$$\mathbf{CaO + CO_2 \leftrightharpoons CaCO_3}$$

$$\Delta_r H_{298K} = -178 \text{ KJ mol}^{-1}$$

Integration of Biomass Within the Cycle



- Potential Issues:
- Combustor: Ash transfer into carbonator if no ash capture step (better efficiency if flue is hot)
- Calciner: potential for bed agglomeration when biomass is used

Making Portland Cement

Mixing and heating of two main materials to form “clinker”

1) A **calcium oxide** containing material (e.g. **limestone/chalk/marl**)
2) An material rich in alumina and silica (e.g. **clay/shale & sand**)

$$CaCO_3 \rightarrow CaO + CO_2$$

$CaO+2CaO.SiO_2$	$\rightarrow 3CaO.SiO_2$	(50-70%) – ‘Alite’	
$2CaO+SiO_2$	$\rightarrow 2CaO.SiO_2$	(15-30%) – ‘Belite’	
$3CaO+Al_2O_3$	$\rightarrow 3CaO.Al_2O_3$	(5-10%)	‘Interstitials’
$4CaO+Al_2O_3 + Fe_2O_3$	$\rightarrow 4CaO.Al_2O_3.Fe_2O_3$	(5-15%)	

Integrating Ca-looping with cement

- Over1 tonne limestone calcined to produce CaO in cement manufacture

- CO_2 emissions come from both burning of fuel and calcination =~ ¾ total

- **Power plants operating with Ca-looping CO_2 capture could provide CaO from waste sorbent, mitigating emissions from both processes.**

- *However - chemical and physical changes in the sorbent may affect quality of the cement produced. Hence the need to manufacture sorbent / clinker in the lab and analyse for trace element content and phase composition / quality.*

- Here, we have looked at the effects of RDF (mainly biomass) and coal on subsequent clinker properties.

Quote from Portland Cement Association:

"The likely concerns from alternative or new natural sources [of raw materials required for cement production] **are the incorporation of trace elements into clinker and their effects on the performance of cement."**

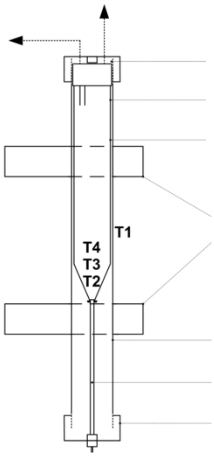
Bhatty, J. I., *Role of Minor Elements in Cement Manufacture and Use, Research and Development Bulletin RD109T*, Portland Cement Association, Skokie, Illinois, U.S.A., 1995.

e.g. ALITE FORMATION:

- Barium: < 0.5 % improves alite formation.
- Boron: above certain concentrations decomposes alite.

- However in our system, introduction of most elements will most likely lead to an improvement in alite formation because of the low baseline level (i.e. using pure oxides and not clay).

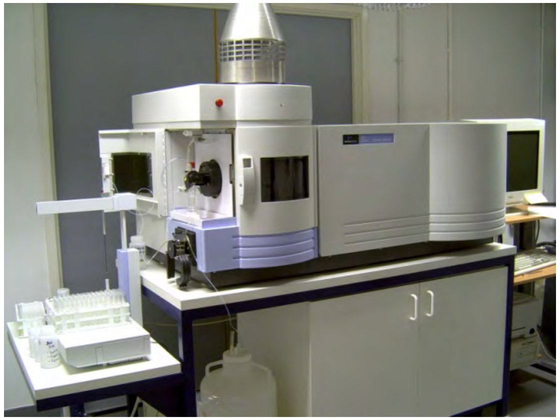
Different stages of lab work



PRODUCTION OF CYCLED SORBENT

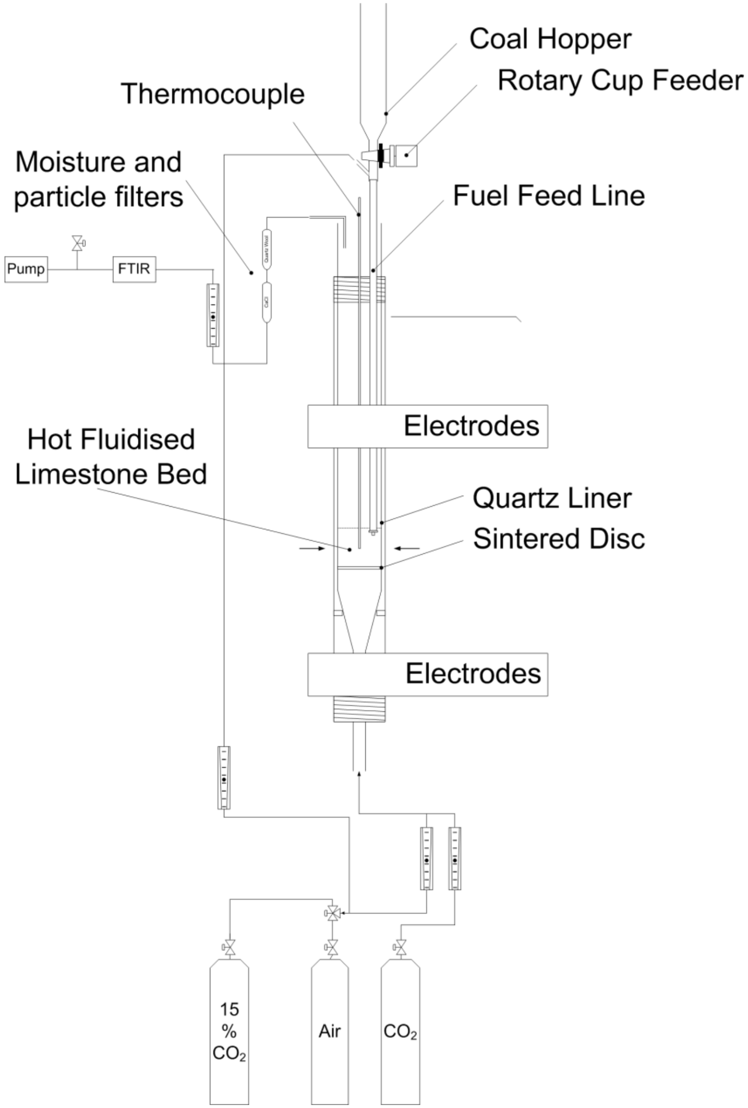
PRODUCTION OF CLINKER

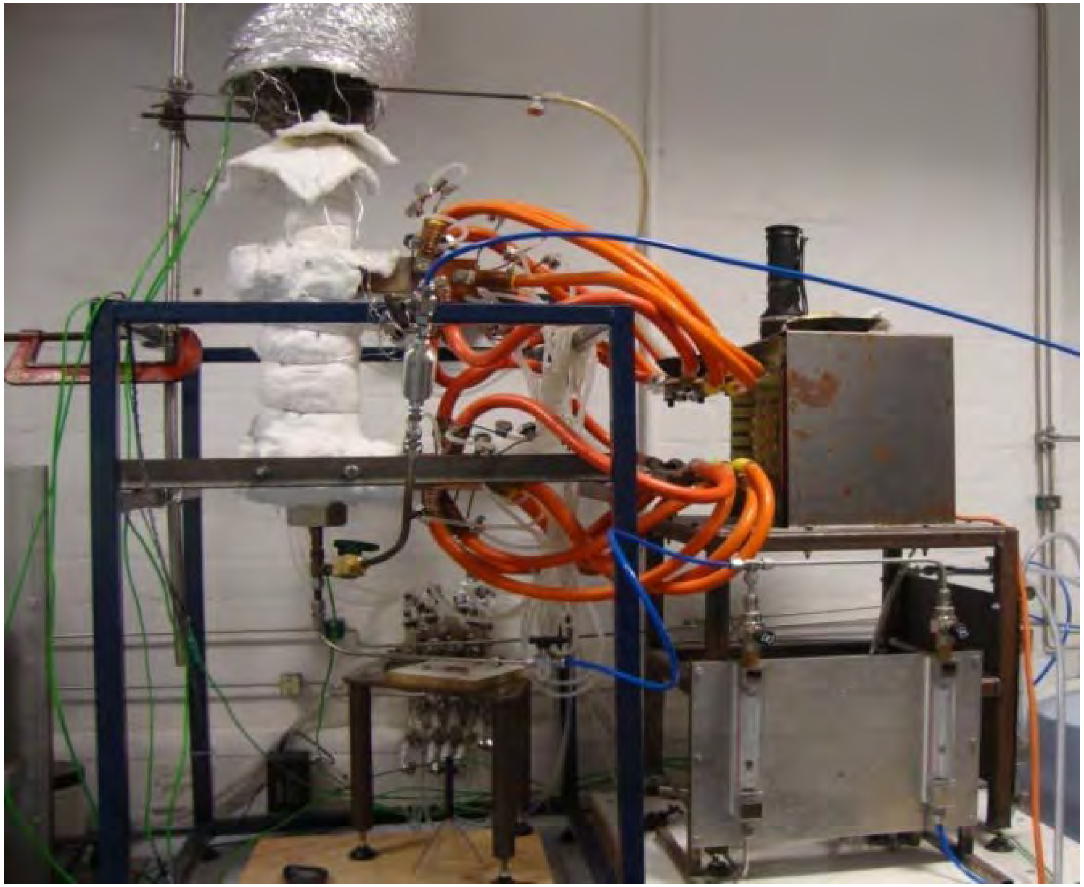
TRACE ELEMENT ANALYSIS OF SORBENT



XRD ANALYSIS OF CLINKER

Rig Schematic: Fluidised Bed with Continuous Coal Feeder





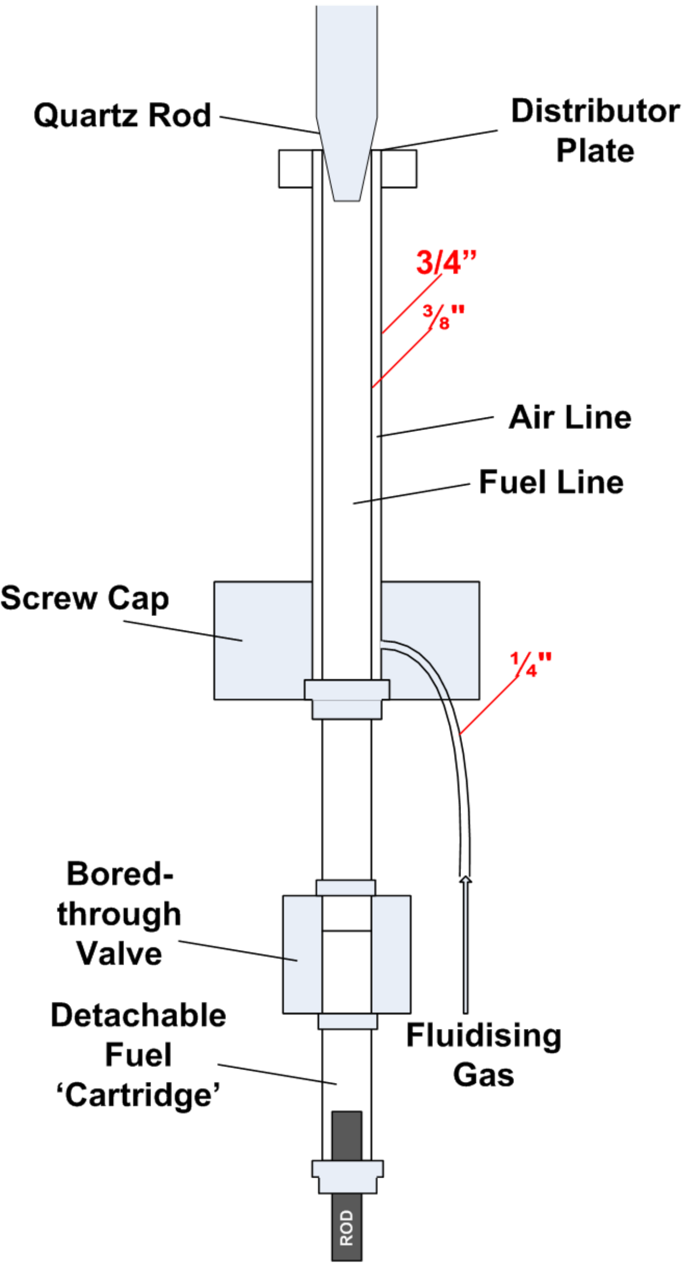
Climafuel feeder

- Novel construction to enable semi-continuous feeding of heterogeneous RDF

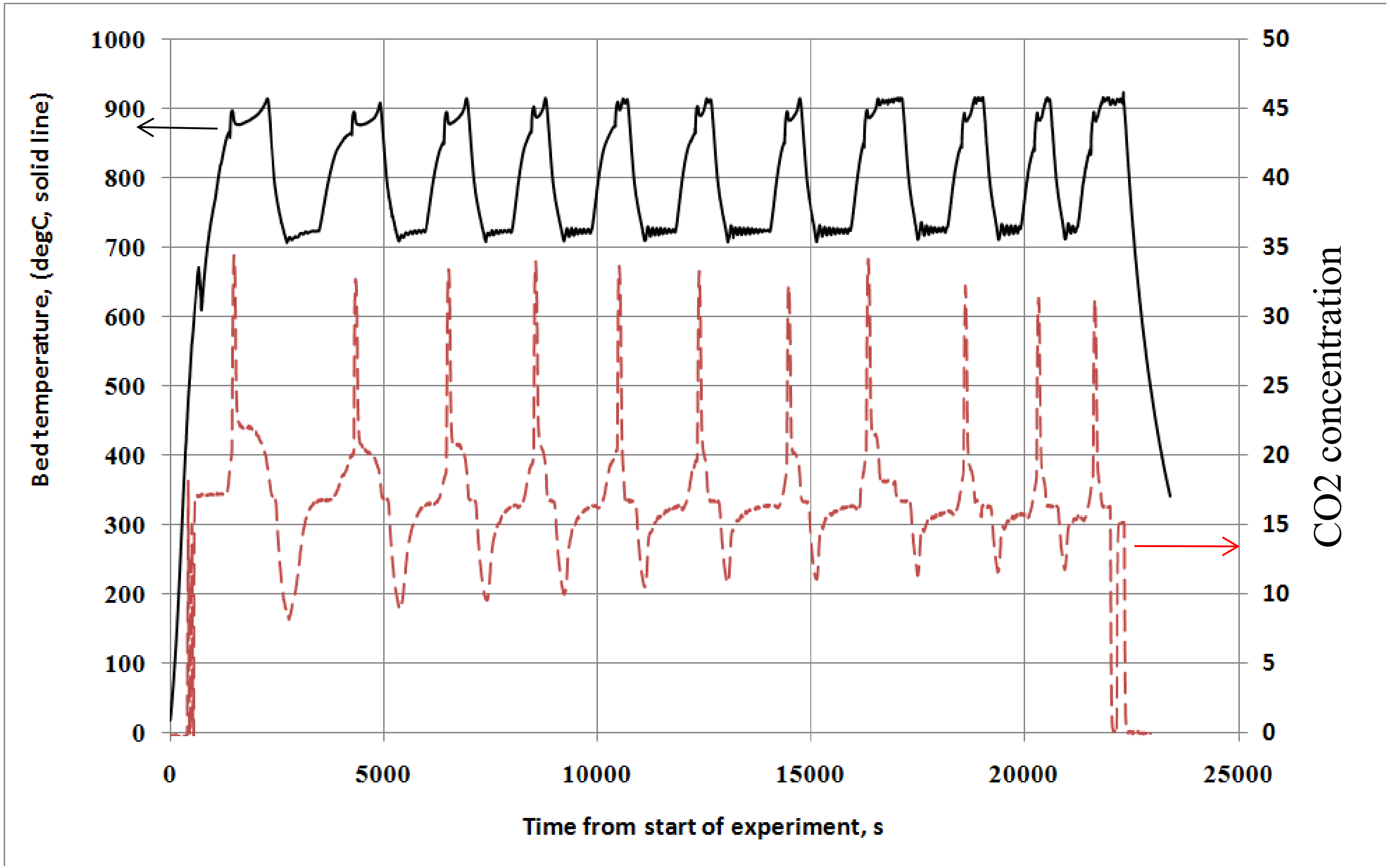
- Pellets made using mould are pushed through central line, cooled by fluidising gas in outside line to prevent pyrolysis during feeding


Original Sample


Pelletised Sample

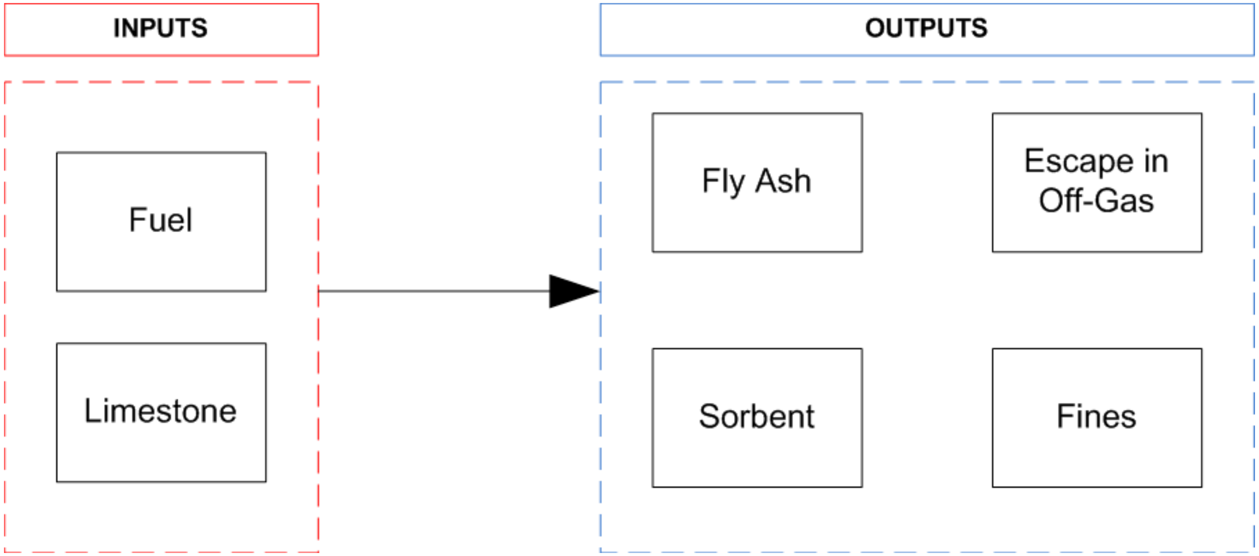


Sorbent Production – A Typical Cycling Experiment



- 15 % CO_2, 5 l /m, Longcliffe 425 – 500 μ limestone.

Partitioning of Trace Elements

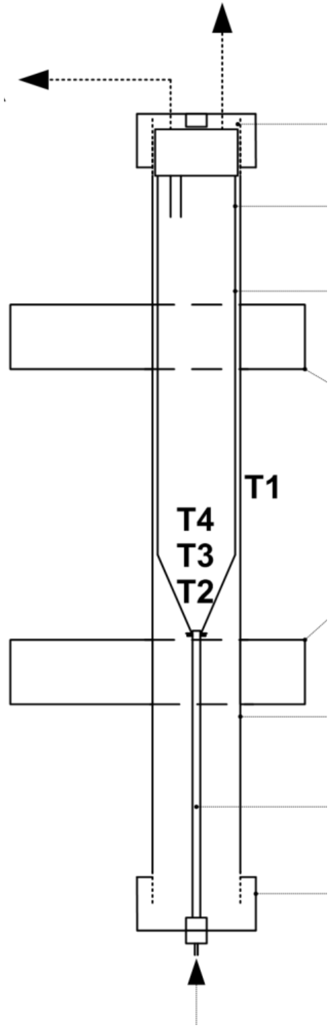


INPUTS

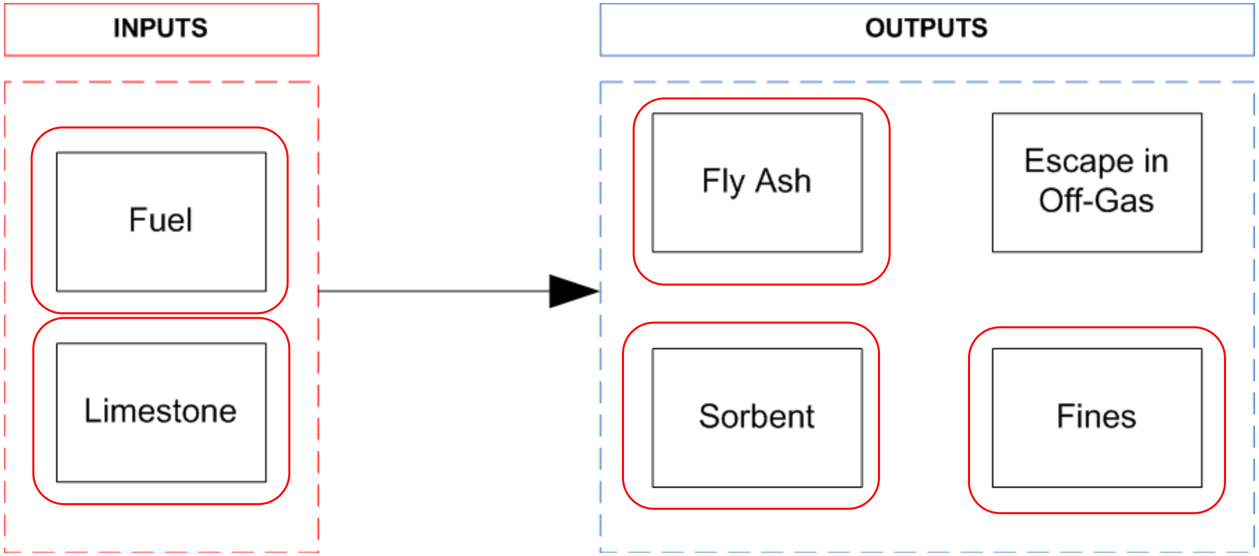
- Fuel
- Limestone

OUTPUTS

- Fly Ash
- Escape in Off-Gas
- Sorbent
- Fines



Partitioning of Trace Elements



INPUTS

Fuel

Limestone

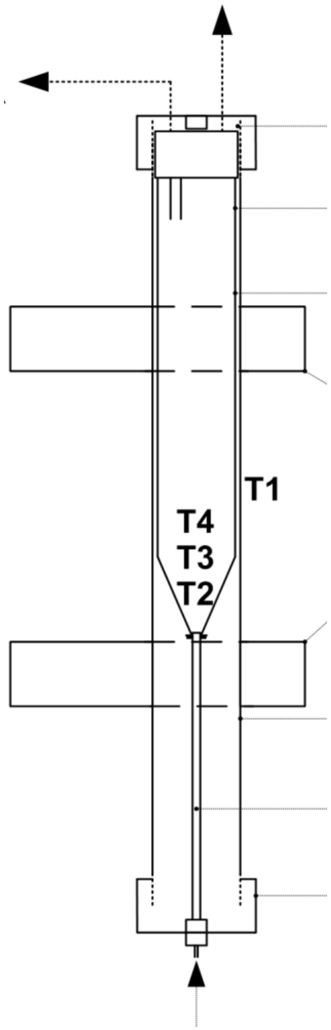
OUTPUTS

Fly Ash

Escape in Off-Gas

Sorbent

Fines

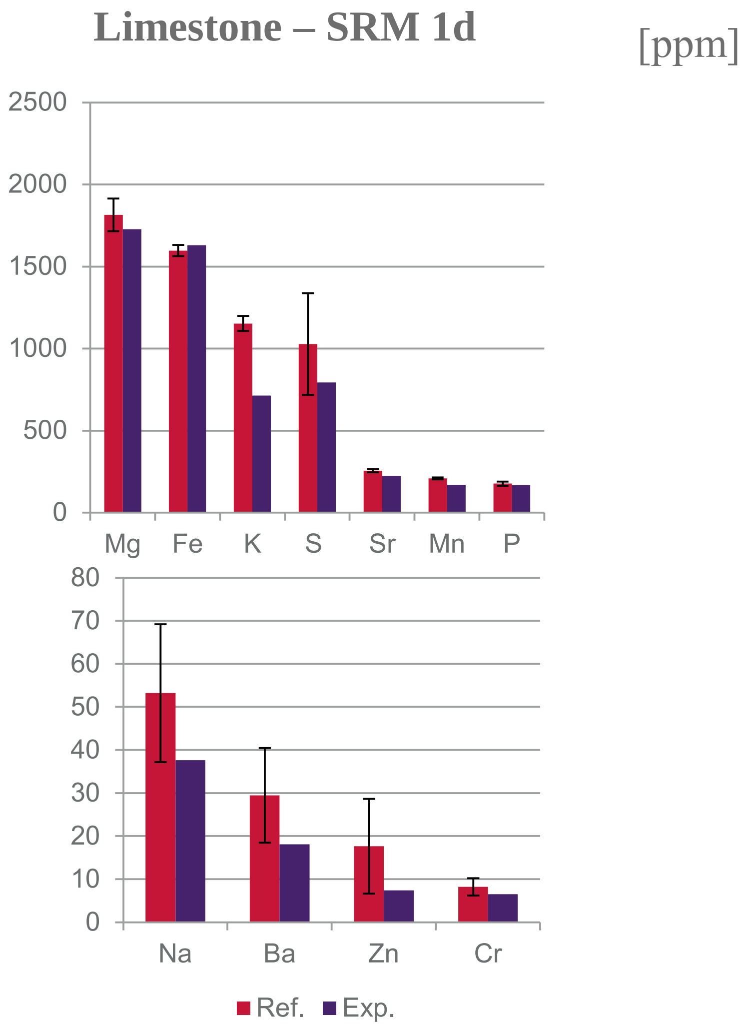


Trace Element Analysis of Fuels & Sorbent

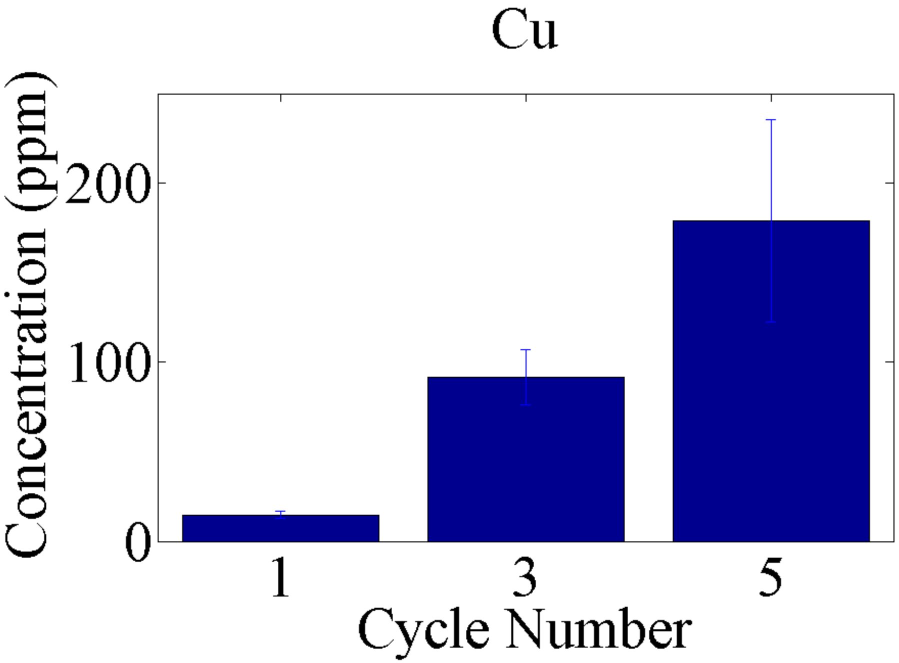
- Inputs (limestone, fuels) and outputs (sorbent, fly ash) materials undergo hot acid digestion, removing mineral matter whilst retaining trace elements in solution ready for ICP.

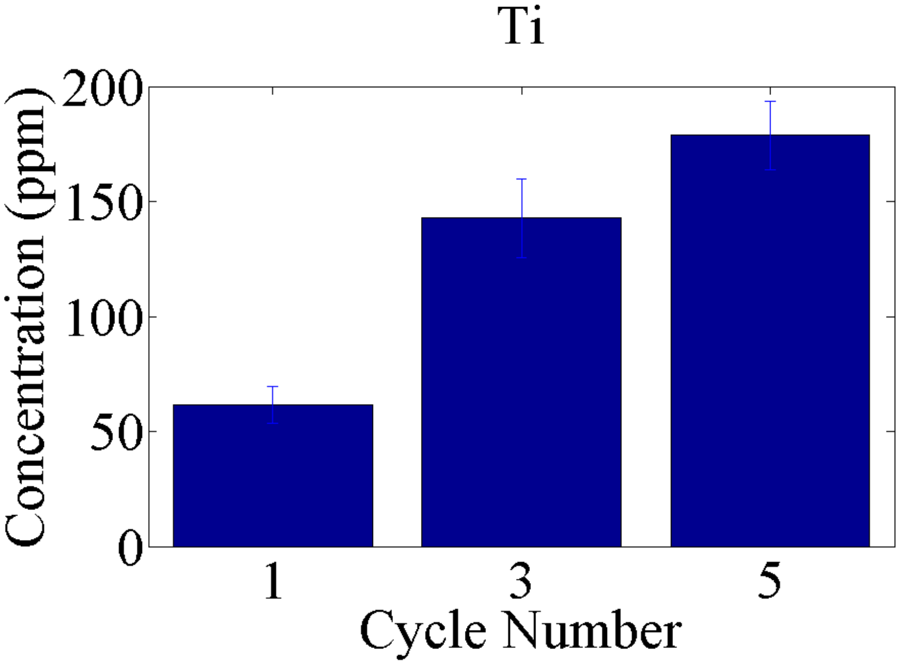
- Digestion methods checked using NIST standard reference materials of similar mineral composition and ideally similar trace element concentrations.

- Plots shown indicate the efficacy of HNO_3 digestion on NIST SRM 1d – most elements are within the errors considered acceptable by the standard.



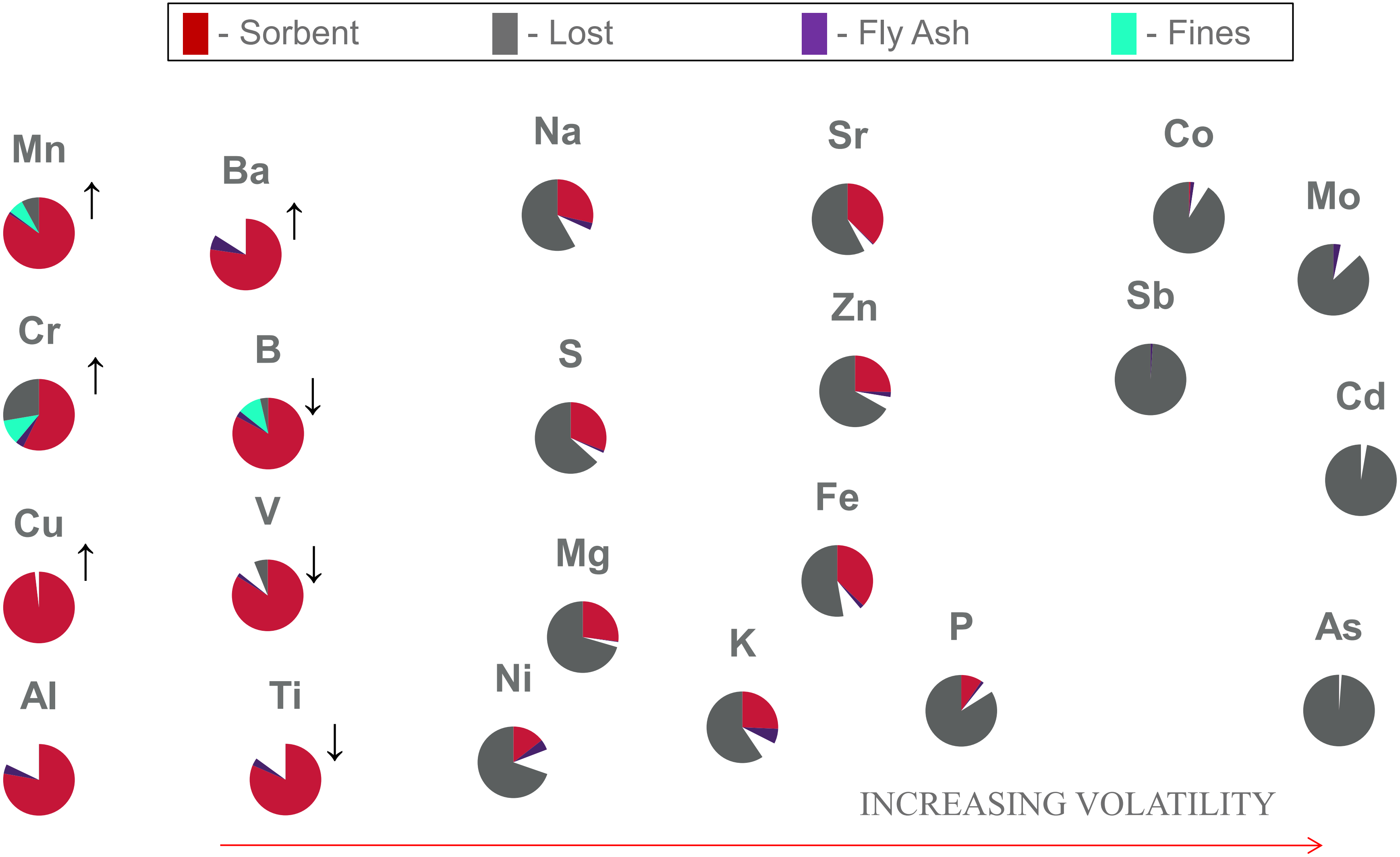
Retention of elements in sorbent from fuel upon cycling: RDF



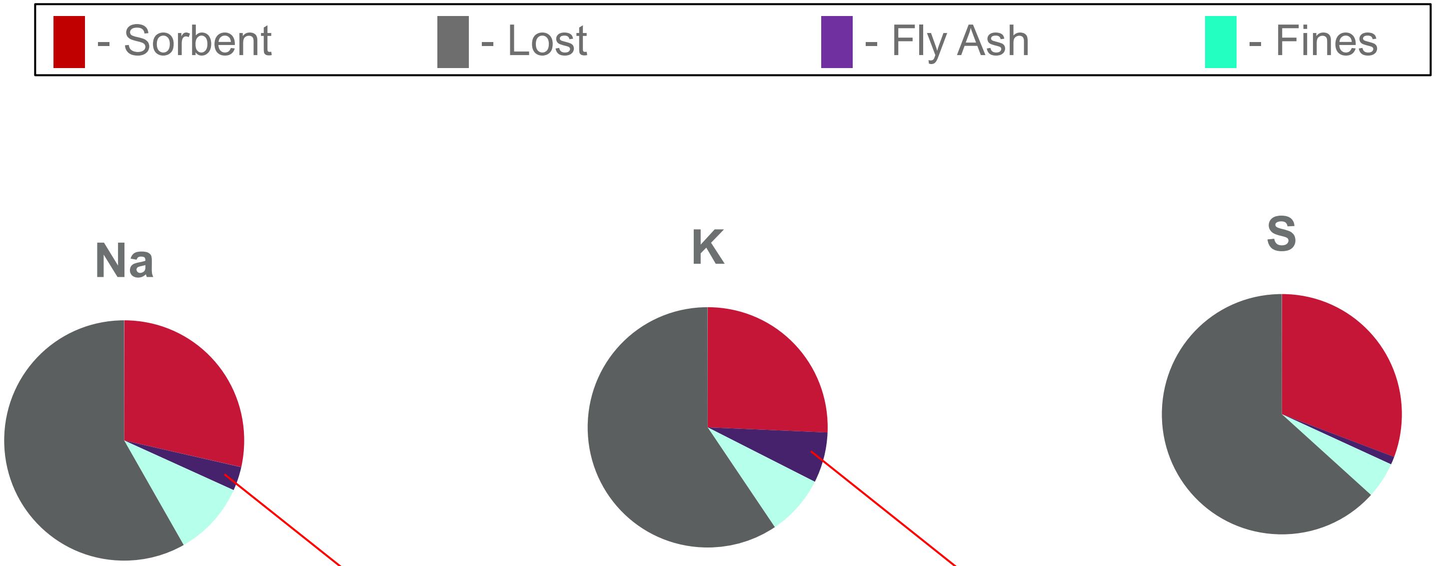


6 g coal added per cycle at a rate of 0.5 g / 60 s

Partitioning of Trace Elements after 5 cycles: Climafuel



Partitioning: Potential Problem Trace Elements



18,000ppm!

20,000ppm!

Imperial College
London

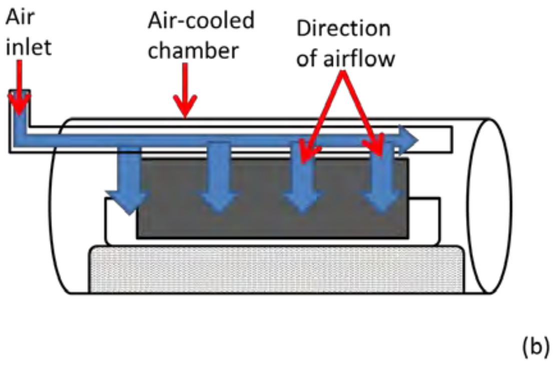
Clinker Production

- CaO sorbent mixed with SiO_2, Al_2O_3 and Fe_2O_3 and fired at 1450°C to produce clinker brick

- Significant initial issues with low cement quality owing to insufficient mixing at the particle scale – solved by compression in a bespoke mould to several tens of bar

- Brick ground to – 45 µ to enable XRD analysis

Clinker Production

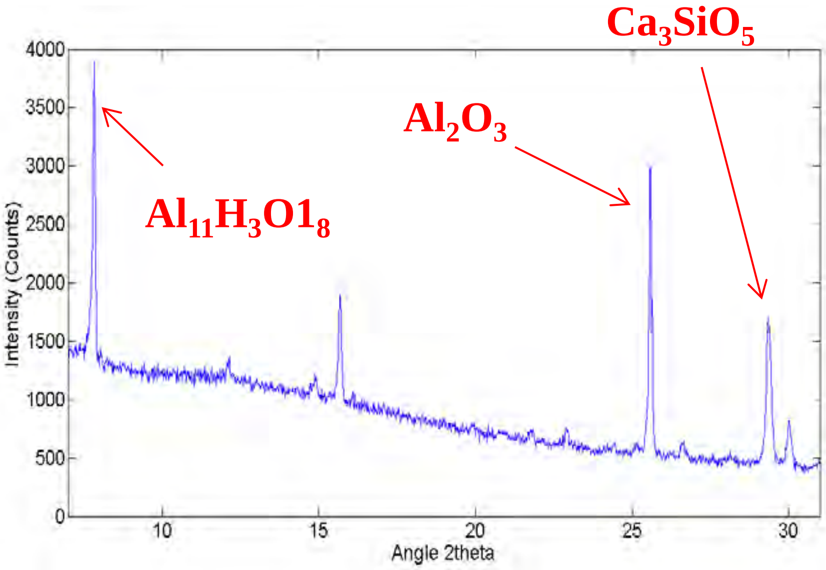


- The brick is then pushed directly from the furnace into an air cooled chamber – 25 l/m applied evenly across brick until ambient temp.

- This is to prevent decomposition of alite to belite which can take place if clinker is allowed to cool at its own rate.

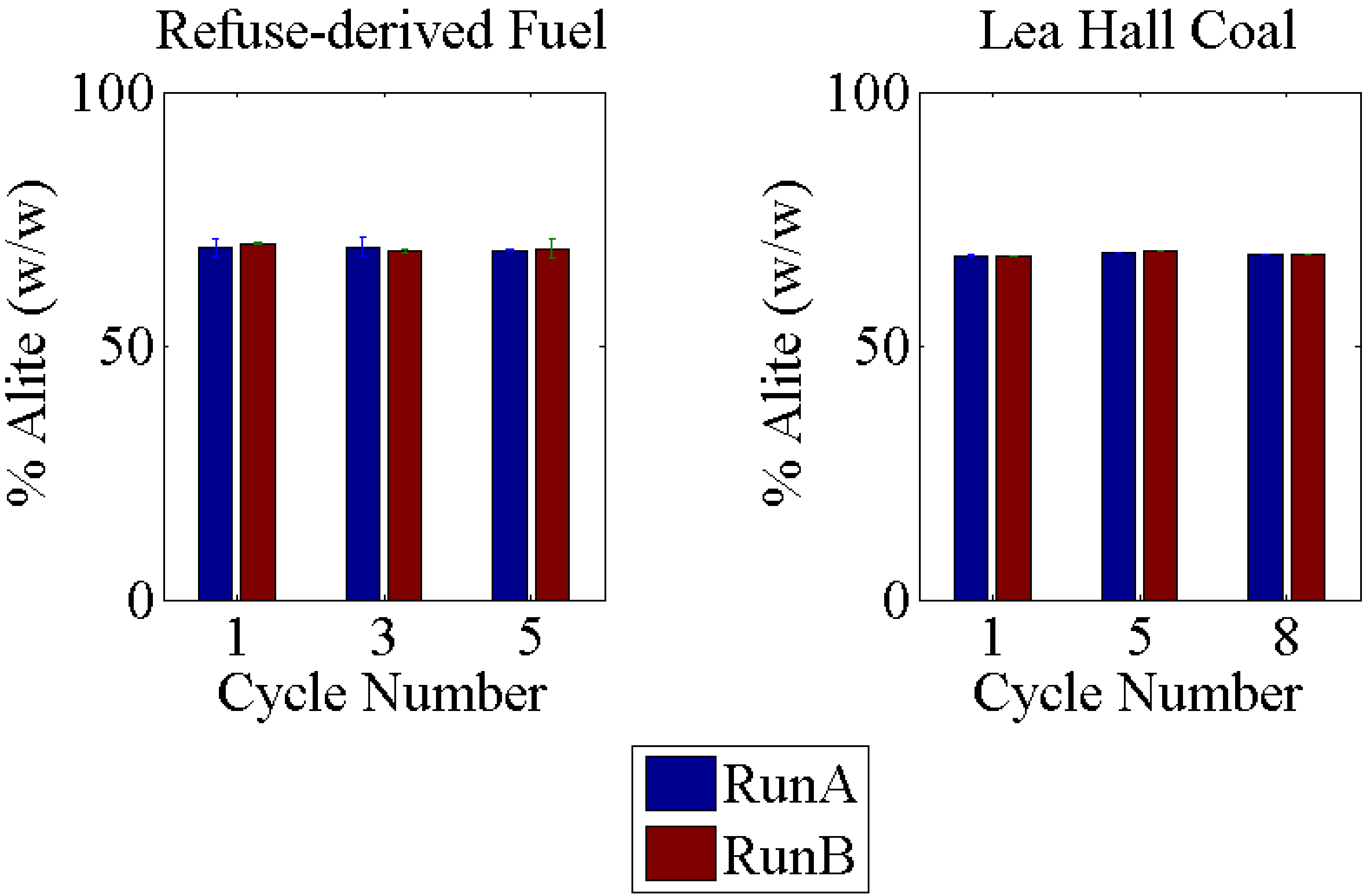
Methods - XRD Analysis of Clinker

- Semi-Quantitative XRD analysis of cement phases using the ‘Generalised Reference Intensity Ratio method’.
- Clinker samples mixed with corundum (Al_2O_3) in 1:1 ratio.
- Comparison of peak areas against RIR values taken from ICDD database give proportion of unknown phase.



$$Xa = (Ia/Ic)*(Irelc/Irela)*(Xc/RIR)$$

% Alite in Clinkers Produced from Cycled Sorbent in Presence of Fuel Combustion



Summary

- Retention of some trace elements in sorbent from fuel upon cycling. Due to low concentrations (ppm levels), no change in % alite detected.
- However trends indicate which elements may affect alite production at higher numbers of cycles (e.g. Boron, Copper and Titanium).
- Mass balances on elements in sorbent indicate some production methods need avoiding, e.g. grinding with metallic components.
- Heavier metals tend to reside in sorbent and will therefore be retained in the cement. Volatile elements leave the system or attach to reactor wall.

Summary (II)

- Next stage is to perform higher numbers of cycles and carry out performance tests to determine possible impact on cement performance using spent sorbent.

- Partitioning shows that the alkalis (**Na** and **K**), though 30-50% retained in sorbent, the remainder leaves the bed as vapours, either collecting as fly ash or leaving in flue gas. This could cause operational problems in the calciner but can be solved using a by-pass line.

- Flowsheeting work once complete will indicate changes to energy demand of producing 1 kg/ck whilst capturing a given amount of CO_2.

Thanks to the EPSRC and Cemex Operations UK Ltd.

Fuel Properties

Analysis	Element (w/w %)	Coal	Biomass
Proximate	Moisture	25.0	50.0
	Fixed Carbon	45.1	0.00
	Volatile Matter	45.7	0.00
	Ash	9.20	6.31
Ultimate	Ash	9.20	6.31
	Carbon	67.1	44.7
	Hydrogen	4.80	5.50
	Nitrogen	1.10	0.00
	Chlorine	0.10	0.00
	Sulphur	1.30	0.00
	Oxygen	16.4	43.5
Sulphur	Pyritic	0.60	0.00
	Sulphate	0.10	0.00
	Organic	0.60	0.00

Emissions Factors with and without Cquestrate

Boiler Configuration	**Calciner Configuration**	**Process Efficiency**	**Emission Factor (g_{CO2}/kWh_e)**	**Average Emission Factor with Cquestrate (g_{CO2}/kWh_e)**
Coal-fired	-	42.4%	**+ 762**	**-**
Co-fired	-	40.9%	**+ 507**	**-**
Biomass -fired	-	39.4%	**0**	**-**
Coal-fired	Coal-fired	27.9%	**+ 55**	**- 70**
Coal-fired	Co-fired	26.8%	**- 158**	**- 283**
Coal-fired	Biomass -fired	26.9%	**- 569**	**- 690**
Co-fired	Coal-fired	27.2%	**- 210**	**- 339**
Co-fired	Co-fired	26.5%	**- 431**	**- 564**
Co-fired	Biomass -fired	26.3%	**- 826**	**- 952**
Biomass -fired	Coal-fired	25.7%	**-719**	**- -862**
Biomass -fired	Co-fired	25.6%	**-934**	**- 1074**
Biomass -fired	Biomass -fired	24.6%	**- 1,404**	**- 1545**