

**POLITECNICO  
DI MILANO**



## **DemoCLOCK Project**

**CLC based power plant: plant arrangement, heat management  
and performance assessment**

**Democlock business brunch, Katowice, December 13th, 2016**

**Paolo Chiesa, Department of Energy, Politecnico di Milano**





## INTRODUCTION

- Few notes about Politecnico di Milano, Italy

## CHEMICAL LOOPING COMBUSTION IN PACKED BED REACTORS

- Heat management
- System operation in power plant and plant performance
- Design and operation of the reactors cluster
- Conclusion



**Politecnico di Milano is a public technical university located in Milan, at the center of the most industrialized area of Italy**

**It is the largest School of Engineering in Italy with over 30'000 students enrolled**

**In the latest QS ranking (year 2016) of the Engineering and Technology universities, Politecnico di Milano ranks 24th in the world, 7th in Europe and 1st in Italy**

**Support to Democlock project has been provided by the Group of Energy Conversion System (GECOS). GECOS staff includes about 40 people, currently involved in 10 FP7 / H2020 running projects and several research activities privately funded by international companies**





## MAIN REMARKS

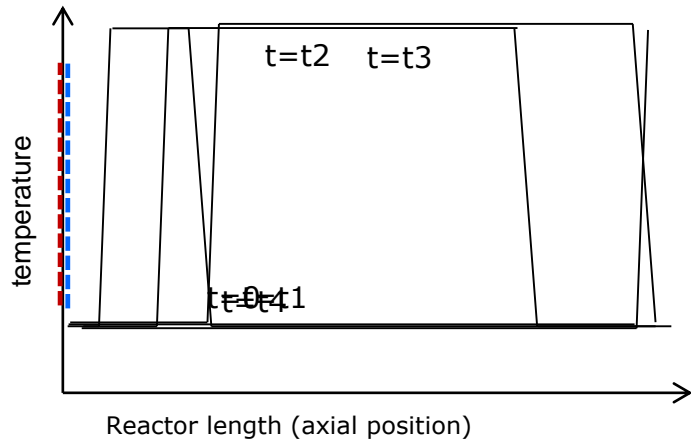
- In Chemical Looping Combustion a metal oxide (acting as oxygen carrier) is placed in contact with a fuel to reduce the metal
- Only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are produced in metal reduction.  $\text{CO}_2$  can be easily separated for storage
- Metal is then oxidized with air. Oxidation of a metal is a very exothermic reaction. Heat released in the reaction can be used for power generation

## OXIDATION OF METAL IN PACKED BED REACTORS

- In packed bed reactors the reaction temperature cannot be controlled by an excess of air flow rate
- Since a large amount of reduced metal is available in the reactor, the reaction proceeds until all the metal is oxidized. More air is fed into the reactor, more heat is released
- Heat released in the reaction is stored inside the bed by increasing the temperature of the bed material

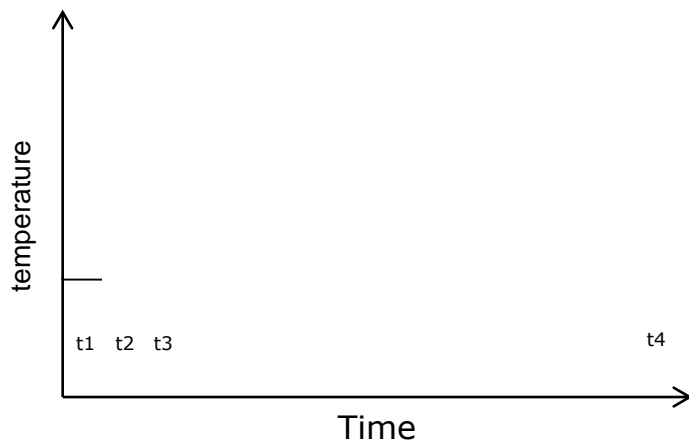


## Temperature profile inside the bed



- Oxidation proceeds faster than heat removal from the bed.
- The reaction front (red dotted line) moves to the right faster than the heat front (blue dotted line).
- Sensible heat stored in the bed can be collected between time  $t_3$  and  $t_4$  for power generation
- **PROBLEM**  
The temperature profile of solids during the reduction phase influences the kinetics

## Temperature of the outlet stream



Spallina V., Gallucci F., Romano M.C., Chiesa P., Lozza G., van Sint Annaland M.: "Investigation of heat management for CLC of syngas in packed bed reactors", *Chemical Engineering Journal*, Volume 225, , Pages 174-191, June 2013, DOI: 10.1016/j.cej.2013.03.054

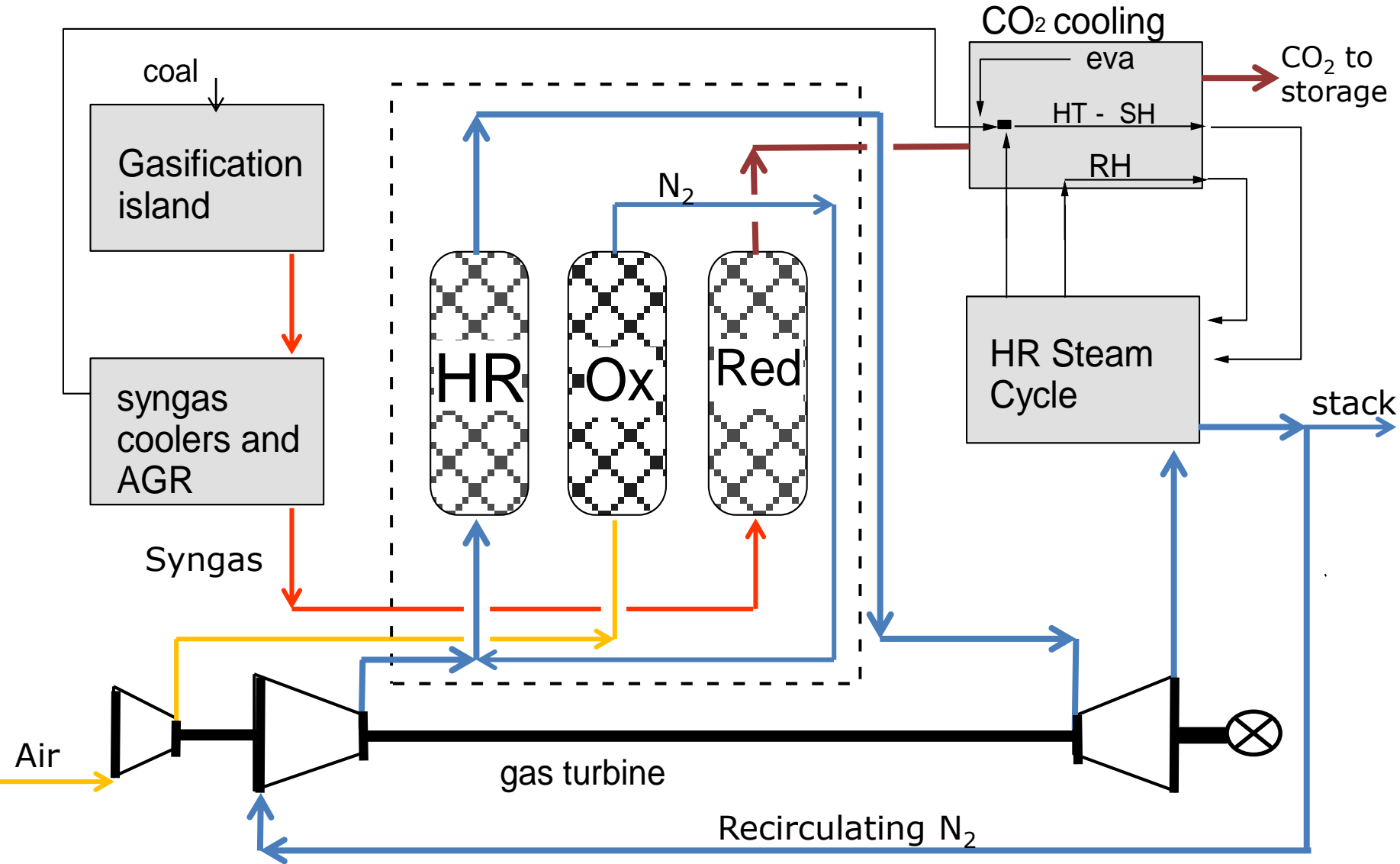


- Ilmenite is used as oxygen carrier because it is cheap and non-toxic
- If CO (included in syngas from coal gasification) is sent over an oxidized ilmenite at low temperature ( $< 900^{\circ}\text{C}$ ), metal reduction is extremely slow
- No matters with oxidation, which occurs fast at any temperature  $> 350^{\circ}\text{C}$
- To cope with this issue, an alternative phase sequence has been devised:
  - 1) After oxidation the bed material is at high temperature
  - 2) Reduction is performed just after oxidation, when the bed is extremely hot.

Metal reduction is a strongly endothermic reaction. It is thermally balanced by simultaneous fuel oxidation, which is exothermic. Bed temperature profile is scarcely affected by this process
  - 3) Heat removal is finally carried out over the reduced bed. An inert stream (composed of  $\text{N}_2$ ) is required to avoid oxidation of the material



# Integration of PBR-CLC in coal-based power plant





# Gasification section

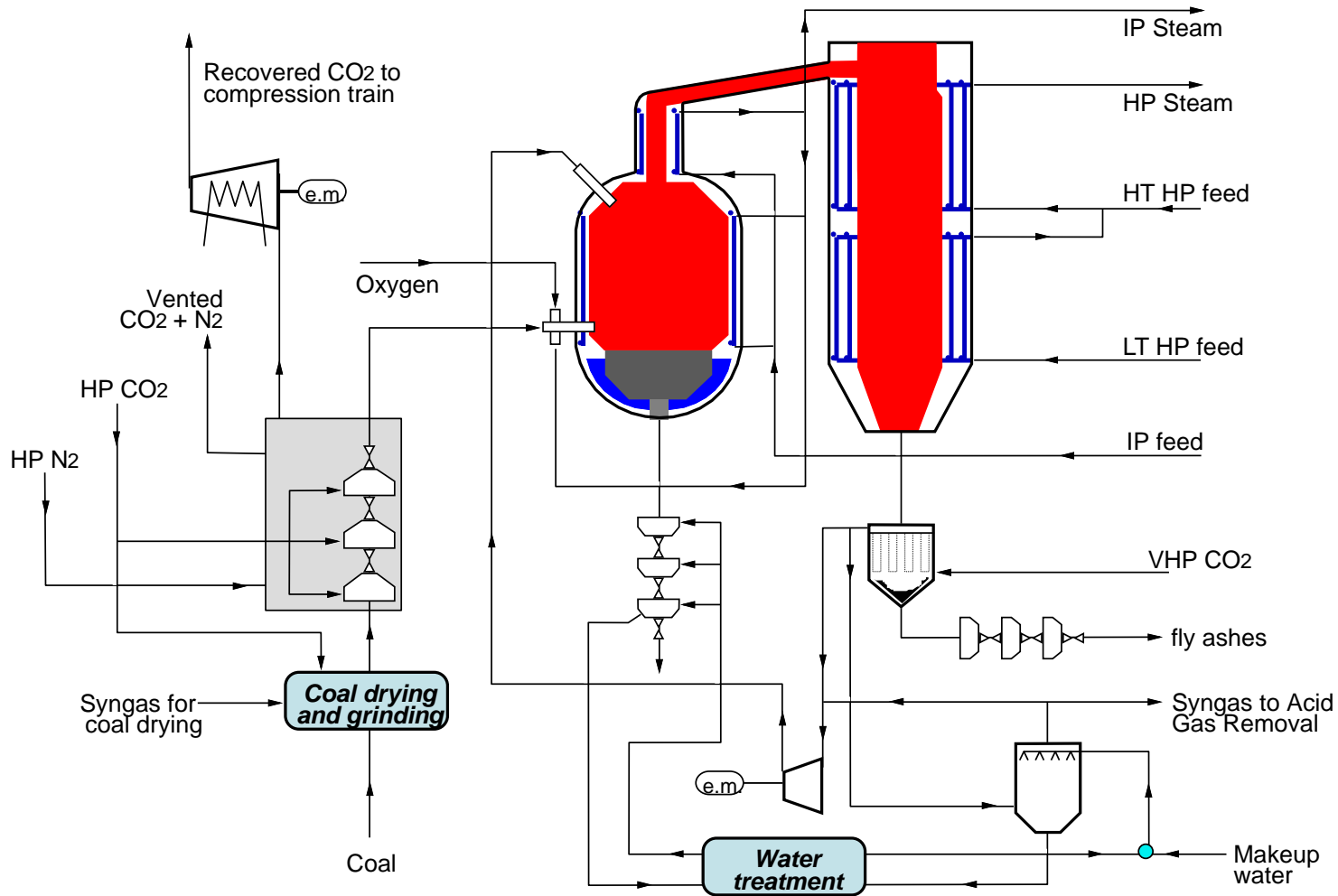


## Shell-type technology:

- Entrained flow reactor
- Dry feed

➤ Oxygen blown

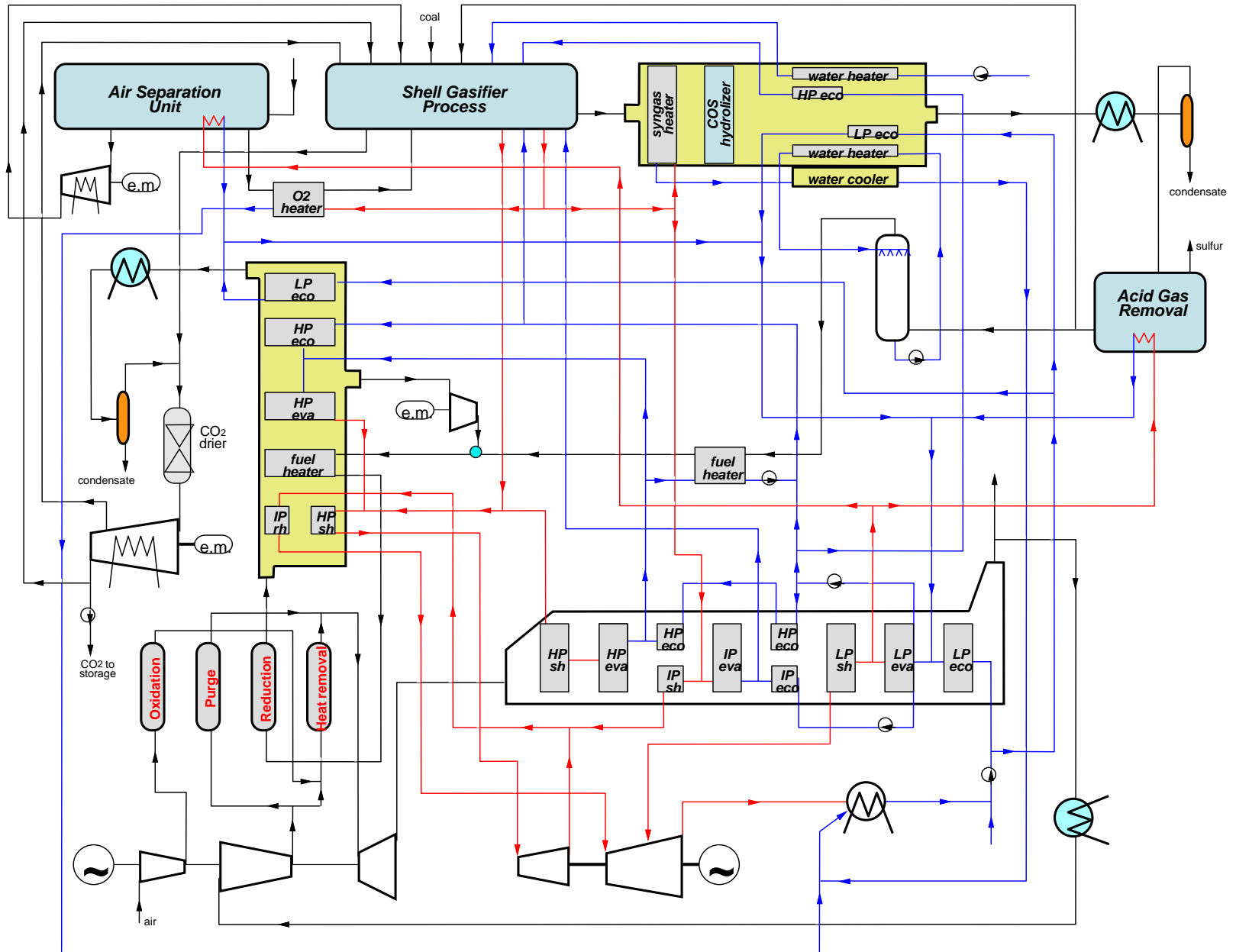
➤ Gas quench + convective syngas cooling for steam generation







# Full plant flow diagram





Coal input [t/h]	122.9
Coal thermal input [ $\text{MW}_{\text{LHV}}$ ]	853.9
Gas Turbine Electric Power Output [MW]	175.2
Steam Turbine Electric Power Output [MW]	240.6
Auxiliary Power Demand [MW]	67.0
Net Electric Plant Output [MW]	348.8
Electric Efficiency [ $\%_{\text{LHV}}$ ]	40.8
CO <sub>2</sub> mass flow rate release to ambient [t/h]	11.7
Specific Emission of CO <sub>2</sub> [g/kWh]	33.5
Carbon Capture Ratio [%]	96.1

~ reference IGCC cycle

Including 75 MW air compressor

34 MW for Air Separation Unit

~ 1/20 of a conventional coal plant

Spallina V., Romano M.C., Chiesa P., Gallucci F., van Sint Annaland M., Lozza G.:  
"Integration of coal gasification and packed bed CLC for high efficiency and near-zero emission power generation", International Journal of Greenhouse Gas Control, Volume 27, Pages 28–41, August 2014  
DOI: 10.1016/j.ijggc.2014.04.029



- A cluster of reactors is required to operate the plant on a continuous duty (oxidation, reduction, heat removal occurring simultaneously in different reactors)
- Temperature of the streams exiting the reactors may vary during time → phases of the single reactor have to be synchronized in order to originate streams at a temperature as constant as possible because rapid changes in temperature can damage the components
- An adequate phase duration is preferable to avoid overstressing the switching system (consisting of piping and valves) and to reduce CO<sub>2</sub> leakages occurring during the phase changes → large amount of metal oxides in the beds
- Low pressure drops on air and N<sub>2</sub> streams to increase the gas turbine performance



## Assumptions:

➤ **Active material fraction in oxidation:  $0.306 \text{ kg}_{\text{active}}/\text{kg}_{\text{solid}}$**   
set to exceed  $1200^\circ\text{C}$  in the oxidation phase

➤ **Reactor void fraction ( $\epsilon$ ) : 40%;**

➤ **Diameter of the spherical particles ( $d_p$ ): 5 mm**

➤ **Solid porosity ( $\alpha$ ) : 40%;**

➤ **Pressure drops by Ergun equation:**

$$\frac{\Delta P}{L} = 150 \cdot \mu \cdot \frac{(1 - \epsilon)^2}{\epsilon^3} \cdot \frac{U}{dp^2} + 1.75 \cdot \frac{(1 - \epsilon)}{\epsilon^3} \cdot \frac{\rho \cdot U^2}{dp}$$

➤ **Minimum duration of oxidation/reduction phase: 15 min.**

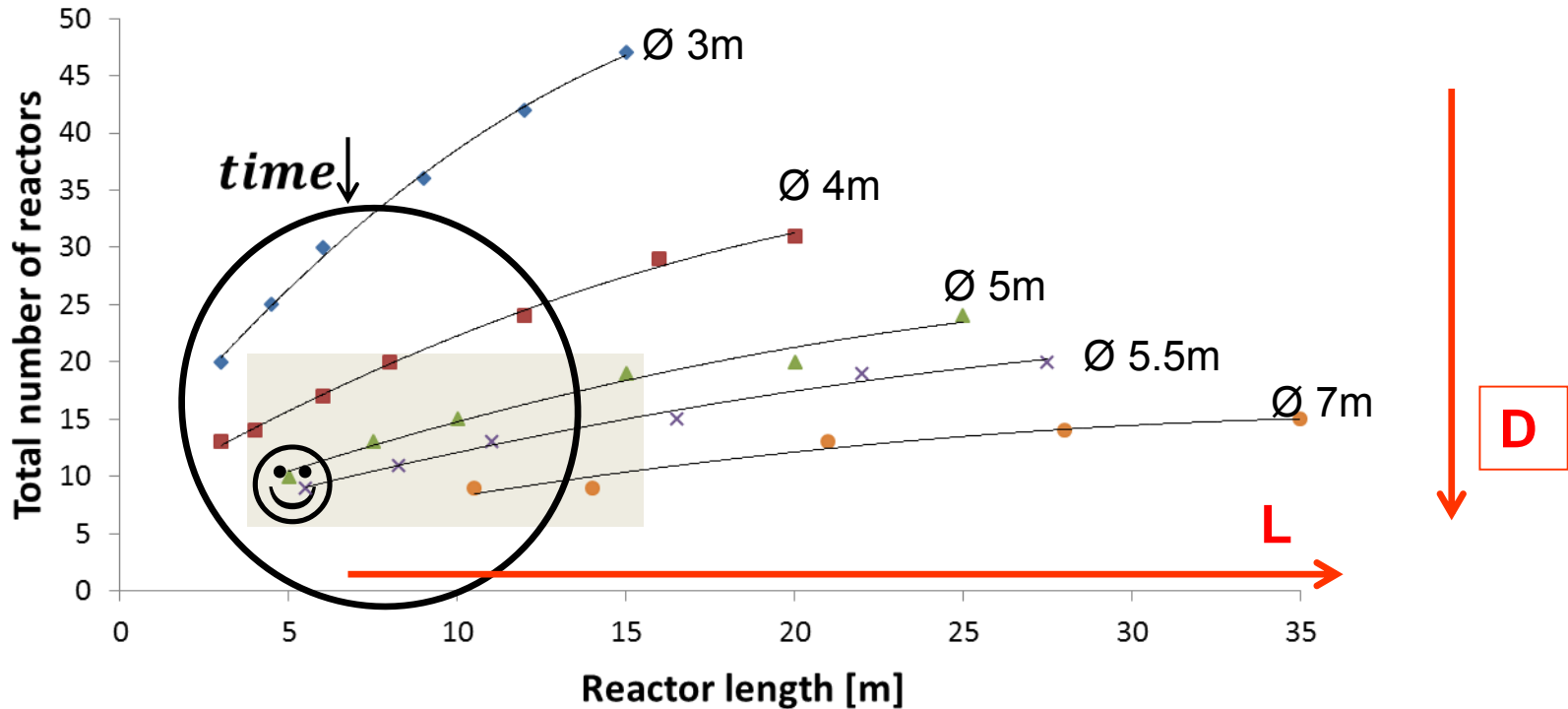
➤ **Geometric constraints:**

**max. internal diameter = 5.5 m    max. reactor length = 20 m**

**min. length to diameter ratio = 1.5**



# Choice of the number of reactors



- Reducing diameter (D):
  - time cycle increases (fluidization starts in the bed) and the number of reactors has to be increased (the total mass flow rate is the same);
  - pressure drops increase and (less mass flow rate have to be used to contain pressure drops)



## Sizing of the reactors cluster for oxidation in co-current mode:

- Number of reactors: 14
- Internal diameter of the reactor: 5.5 m
- Length of the reactor bed: 11 m

Phase	$N_{\text{reactors}}$	$\dot{m} \left[ \frac{\text{kg}}{\text{s}} \right]$	$\tau \text{ [s]}$	$\Delta P / P_{\text{in}} \text{ [%]}$
Oxidation	3	59.3	1028	4.77
Purge *	1	30.5	343	1.48
Reduction	3	49.3	1028	3.90
Heat Removal	7	75.7	2380	7.51

\* Purge phase required is required to flush oxygen from the reactor before reduction to prevent explosions

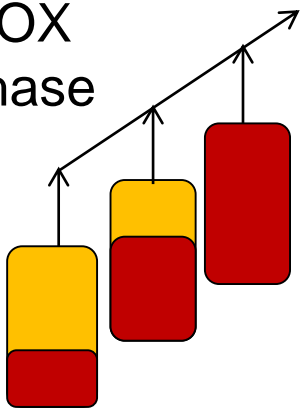
- ❖ Lower number of reactors by increasing the particle diameter ( $d_p$ )
- ❖ Similar results are obtained for counter-current oxidation feed

Spallina V. Chiesa P., Martelli E., Gallucci F., Romano M.C., Lozza G., van Sint Annaland M.: "Reactor design and operation strategies for a large-scale packed-bed CLC power plant with coal syngas", International Journal of Greenhouse Gas Control, vol. 36, p. 34-50, May 2015  
DOI: 10.1016/j.ijggc.2015.01.025



# Operation of the reactors cluster

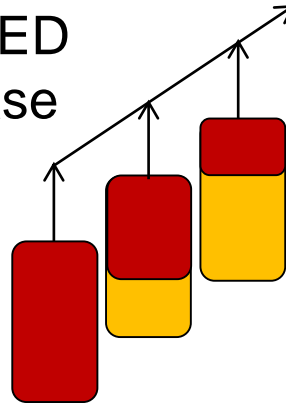
3 OX phase



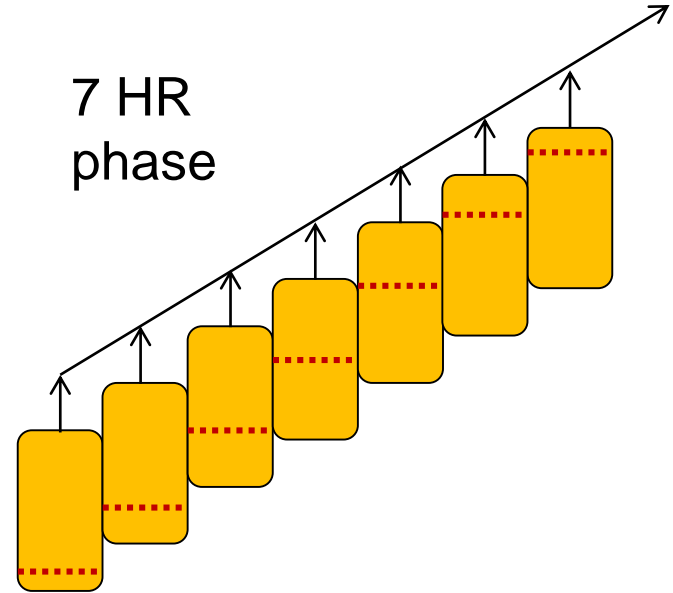
1 Purge phase



3 RED phase



7 HR phase

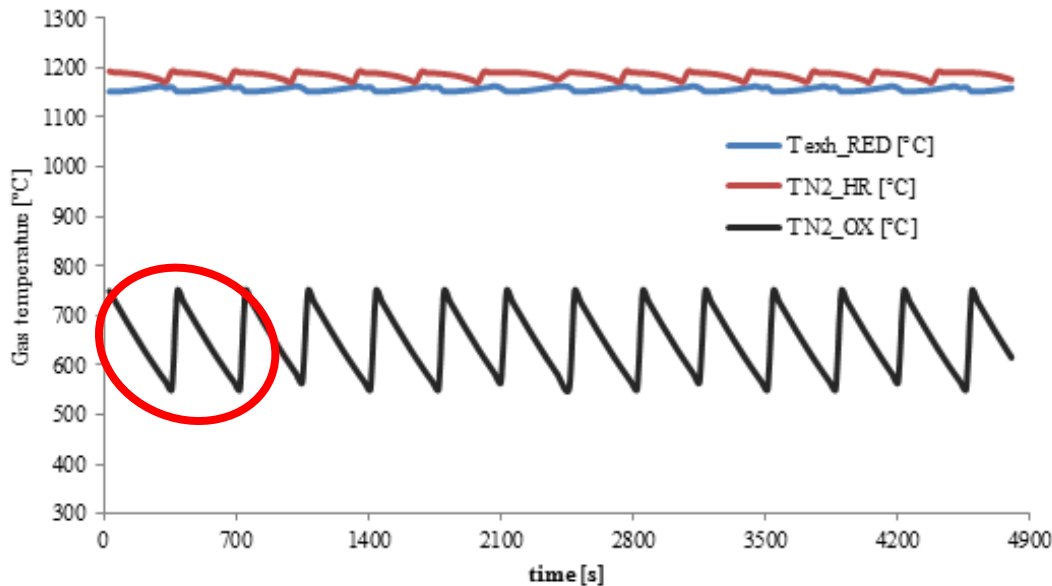
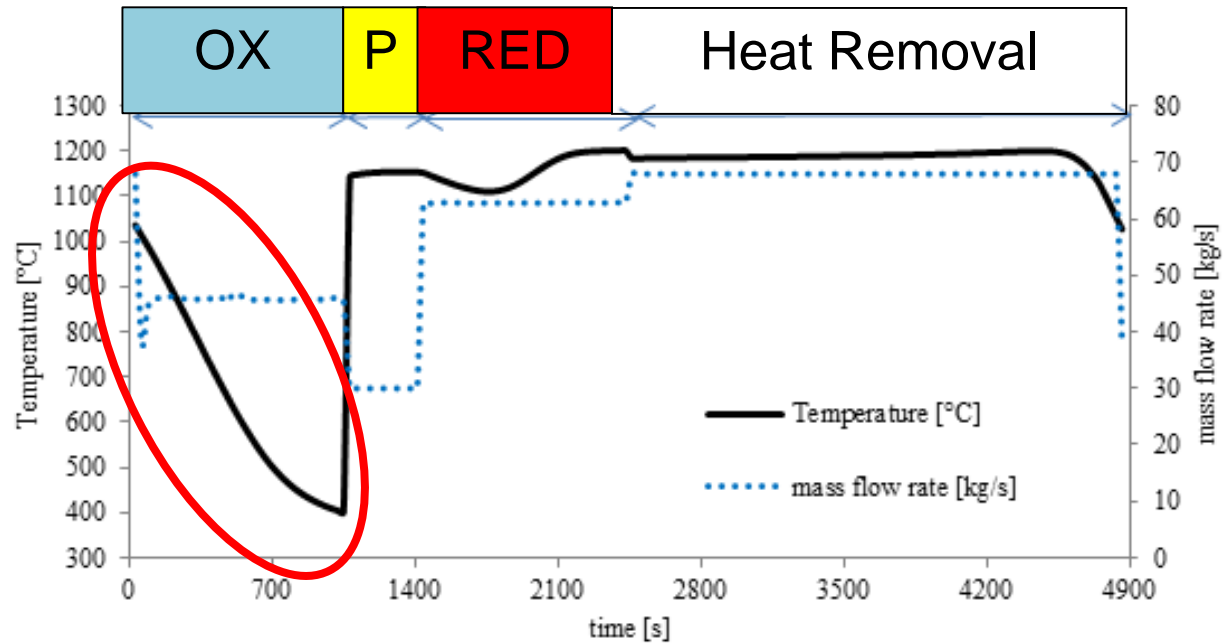


D 5.5	L 11	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14	
τ	τ/3	OXI	HR	HR	HR	HR	HR	HR	HR	HR	RED	RED	RED	PURGE	OXI	OXI
	τ/3	OXI	OXI	HR	HR	HR	HR	HR	HR	HR	HR	RED	RED	PURGE	OXI	OXI
	τ/3	OXI	OXI	OXI	HR	HR	HR	HR	HR	HR	HR	RED	RED	RED	PURGE	PURGE
τ	τ/3	PURGE	OXI	OXI	OXI	HR	HR	HR	HR	HR	HR	HR	RED	RED	RED	RED
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	τ/3	HR	HR	HR	HR	HR	HR	HR	RED	RED	RED	PURGE	OXI	OXI	OXI	OXI



# Evolution of temperature

## Single reactor



## Cluster of reactors





- **Chemical Looping Combustion in Packed Bed Reactor is a promising technology for high efficiency coal power plant with near-zero CO<sub>2</sub> emissions**
- **The main advantages of pressurized CLC is the low energy consumption for CO<sub>2</sub> separation and compression**
- **Choice of ilmenite as oxygen carrier is convenient for low cost and non-toxicity**
- **The slow kinetics of ilmenite in the reduction phase imposes a proper heat management of the reactors cluster to match the requirements of a power cycle**



Thank You!  
Questions?