

CLEAN ClinkER by calcium
looping for low-CO₂ cement

CLEAN ClinkER



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8th High Temperature Solid Looping Cycles Network Meeting

CLEANKER Overview

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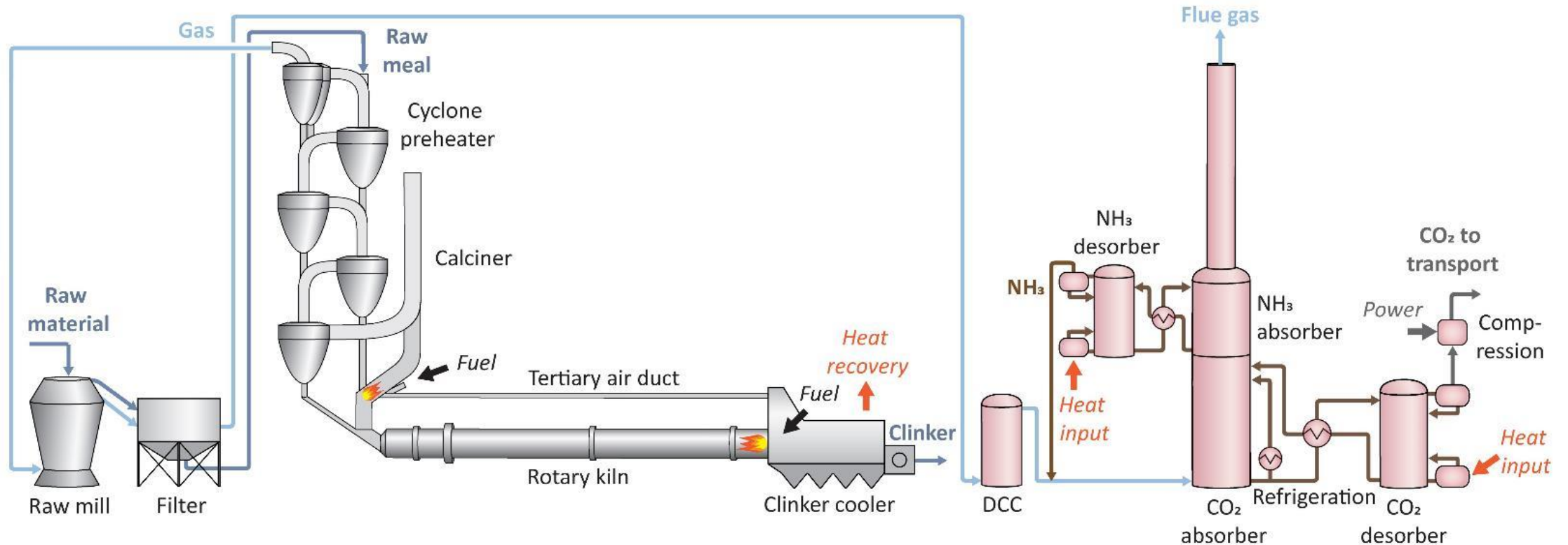
- **Main technologies for CO₂ capture in cement plants:**
 - Post-combustion solvent systems
 - Oxyfuel
 - Externally heated calcination
 - Calcium looping

- **CLEANKER project**
 - Project objectives
 - The consortium
 - CaL integrated configuration
 - CLEANKER demo system
 - CLEANKER project timeline
 - CLEANKER targets







Post-combustion capture by solvents

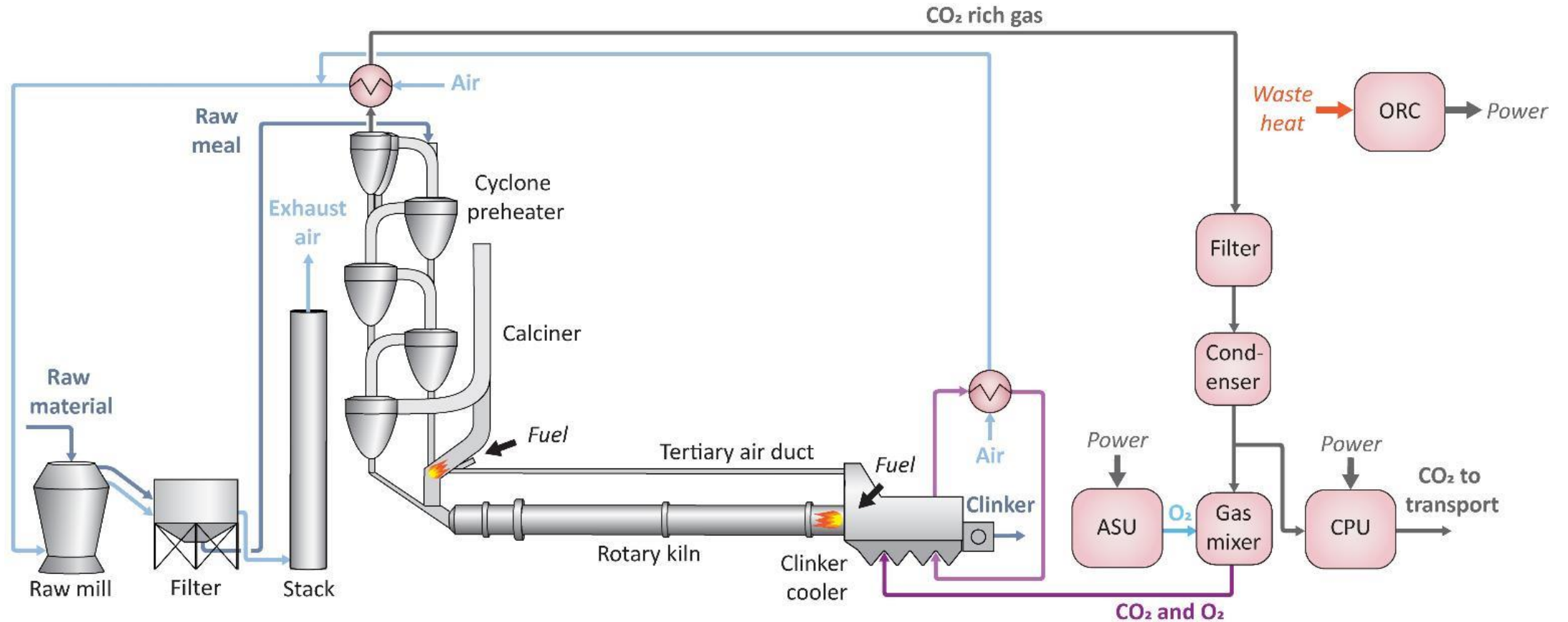
- Most mature technology for full-scale applications. Large scale units operating on power plant flue gases.
- Extensive experience for application in power plants



Post-combustion capture by solvents

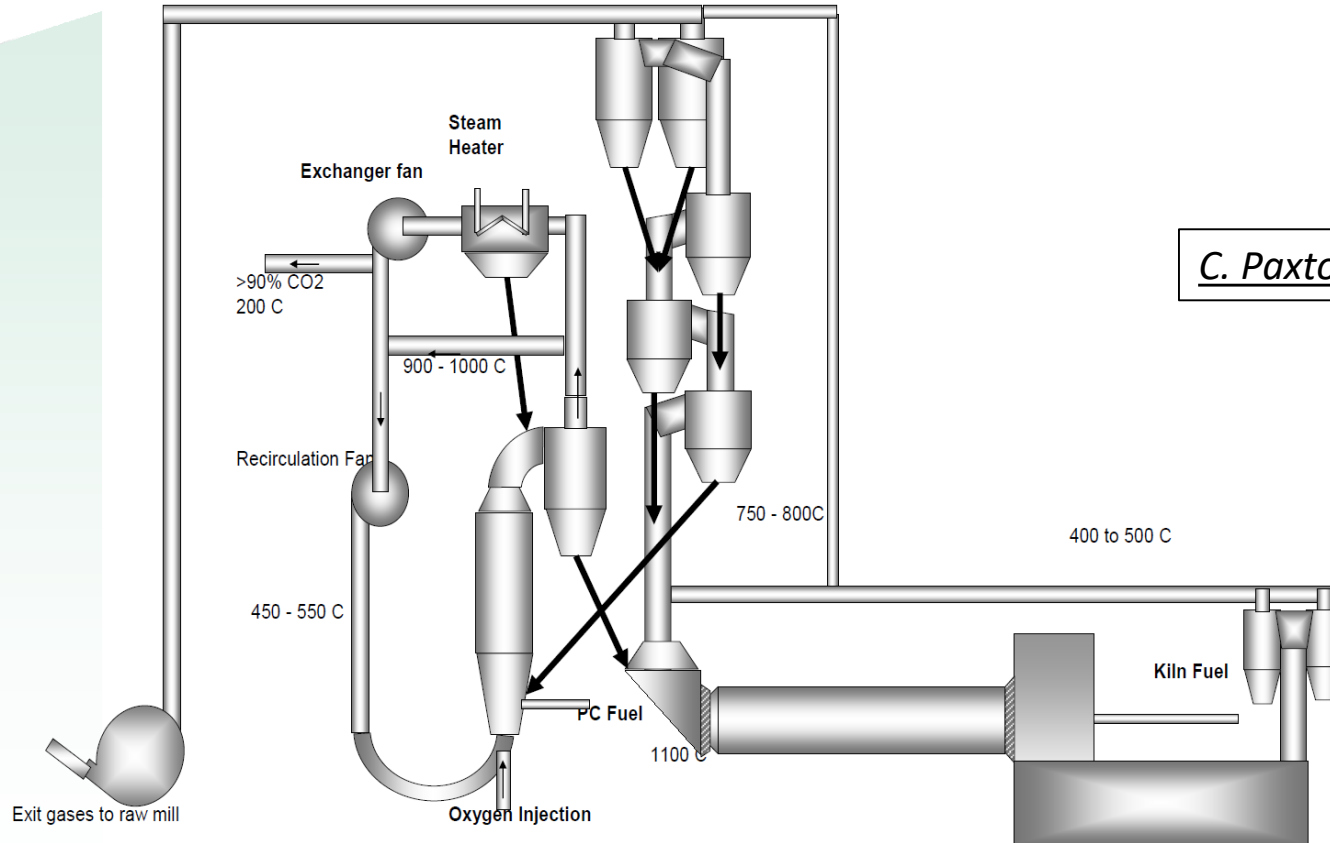
- Most mature process for industrial applications. Large scale units operating on power plant flue gases (corresponding to full-scale cement kiln gas). 
- With MEA, deep SO₂ removal needed to avoid solvent degradation 
 - gas desulfurization required.
- Some emissions of amines and NH₃ expected. 
- High thermal power needed for solvent regeneration: ~2-4 MJ/kgCO₂
 - in a 120 t/h clinker plant generating 850 kgCO₂/tclinker, 80-105 MWth at about 120°C are needed for capturing 90% of the CO₂. 
 - Dedicated steam generation unit needed.

Oxyfuel combustion



Oxyfuel combustion

- Partial oxyfuel: oxyfuel pre-calciner with air-fired rotary kiln and air-cooled clinker cooler



C. Paxton, M. Weichinger, 2008. Patent WO2008059378 A2.



Oxyfuel combustion

- Partial oxyfuel

- Maximum CO₂ capture efficiency limited at 60-70%
- No modifications of the rotary kiln operation and of the clinker cooler
- Not affected by false air ingress in the rotary kiln and clinker cooler

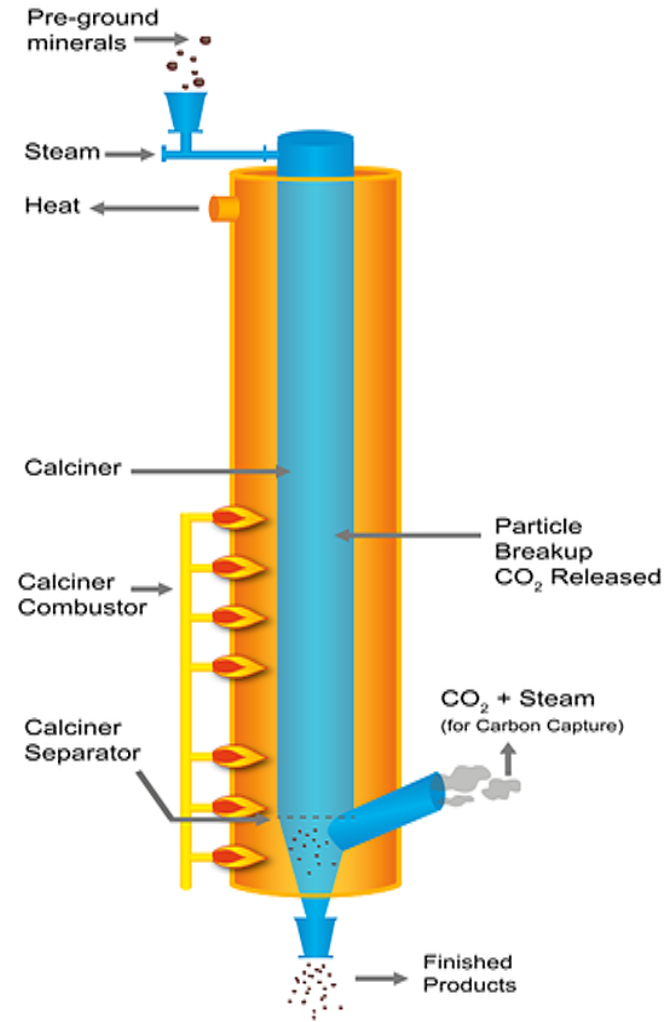


- Full oxyfuel (oxyfuel pre-calciner + oxyfuel rotary kiln):

- Maximum CO₂ capture efficiency > 90% possible
- Tight sealing needed in the rotary kiln and clinker cooler to keep very low air infiltration and avoid CO₂ dilution





Externally heated calcination



www.project-leilac.eu/



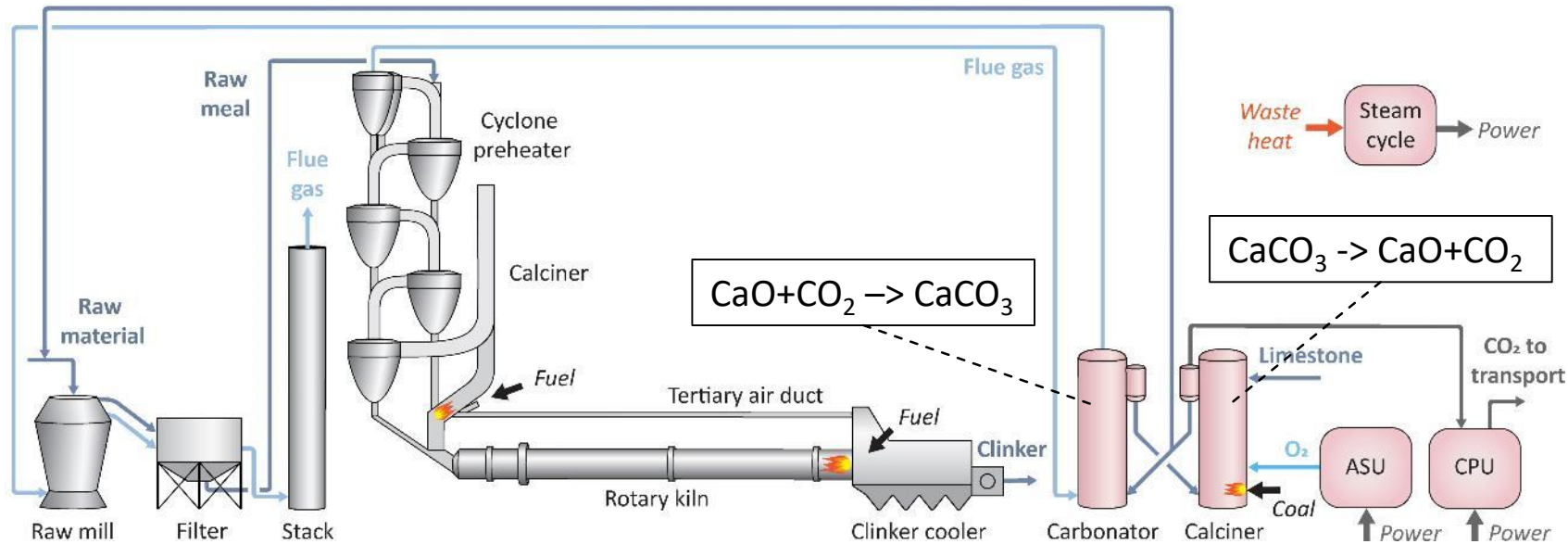
Externally heated calcination

- High purity CO₂ produced 
- No ASU, no chemicals 
- Challenging scalability: very high heat transfer surface needed in full-scale cement kilns 
- Limited capture efficiency: only CO₂ from limestone calcination is captured 
 - Hybridization needed to achieve high capture efficiency
- Calcination restricted to clean fuels to avoid fouling of heat transfer surface 

Calcium Looping

• Tail-end Calcium looping:

- Post-combustion capture configuration -> highly suitable for retrofit
- High fuel consumption (double calcination for the mineral CO₂ captured)
- Heat from fuel consumption recovered in efficient (~35% efficiency) steam cycle for power generation
- CFB CaL reactors: d₅₀=100-250 μm, vs. particle size for clinker production d₅₀=10-20 μm -> CaL purge milled in the raw mill at low temperature



Arias et al., 2017. Ind. Eng. Chem. Res., 56, 2634–2640;
Hornberger et al., 2017. Energy Procedia, 114, 6171–6174;
De Lena et al., 2017. Int. J. Greenh Gas Control, 67, 71-92.

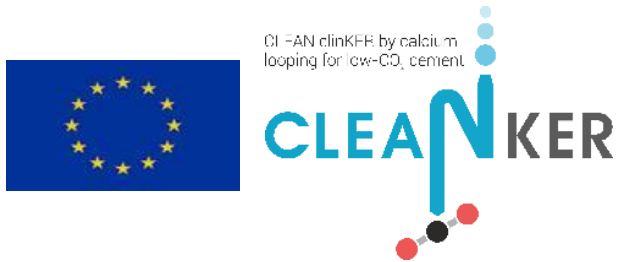
CEMCAP



Calcium Looping

Integrated CaL:

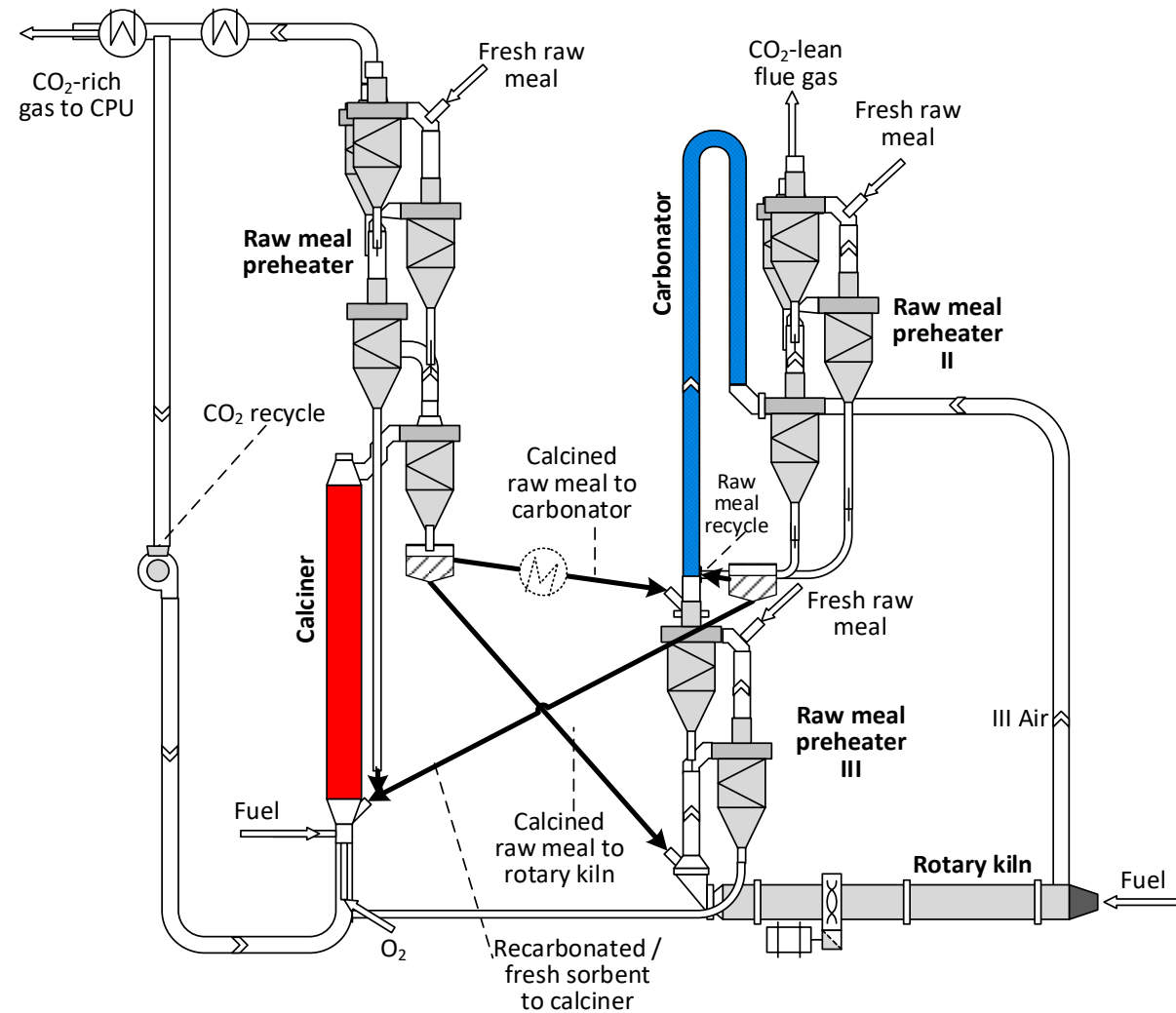
- CaL carbonator highly integrated within the preheater, captures CO₂ from rotary kiln gas
- CaL calciner coincides with the cement kiln pre-calciner -> no double calcination, lower fuel consumption
- Calcined raw meal as CO₂ sorbent in the carbonator instead of high purity limestone
- Sorbent has small particle size ($d_{50}=10-20 \mu\text{m}$) -> entrained flow reactors



Alonso et al., 2018. Energy & Fuels, 31, 13955–13962.

Turrado et al., 2018. Ind Eng Chem Res, 57, 13372-13380.

De Lena et al., 2019. Int J Greenh Gas Control, 82, 244-260.






Calcium looping

- Tail-end configuration:

- Low uncertainty in the feasibility of the process (very similar to application in power plants) 
- Very high CO₂ capture can be achieved 
- Double calcination leads to high fuel consumptions 

- Integrated CaL configuration:

- High CO₂ capture efficiency without modifying rotary kiln operation (no need of kiln oxyfiring). 
- Higher thermal efficiency and lower fuel consumptions expected (compared to option 2) 
- New carbonator design and fluid-dynamic regime: fluid-dynamics, heat management and sorbent performance need verification 

Key Performance Indicators

- Equivalent primary energy consumption:

$$q_{eq} \left[\frac{MJ}{t_{clinker}} \right] = q + \frac{P_{el}}{\eta_{ref,el}}$$

Direct fuel consumption

Indirect fuel consumption
 Average European grid: $\eta_{ref,el} = 45.9\%$

- Equivalent CO₂ emissions:

$$e_{CO_2,eq} \left[\frac{kg_{CO_2}}{t_{clinker}} \right] = e_{CO_2} + P_{el} \cdot e_{ref,el}$$

Direct emissions

Indirect emissions
 Average European grid: $e_{ref,el} = 262 \text{ kg/MWh}$

Qualitative technology comparison

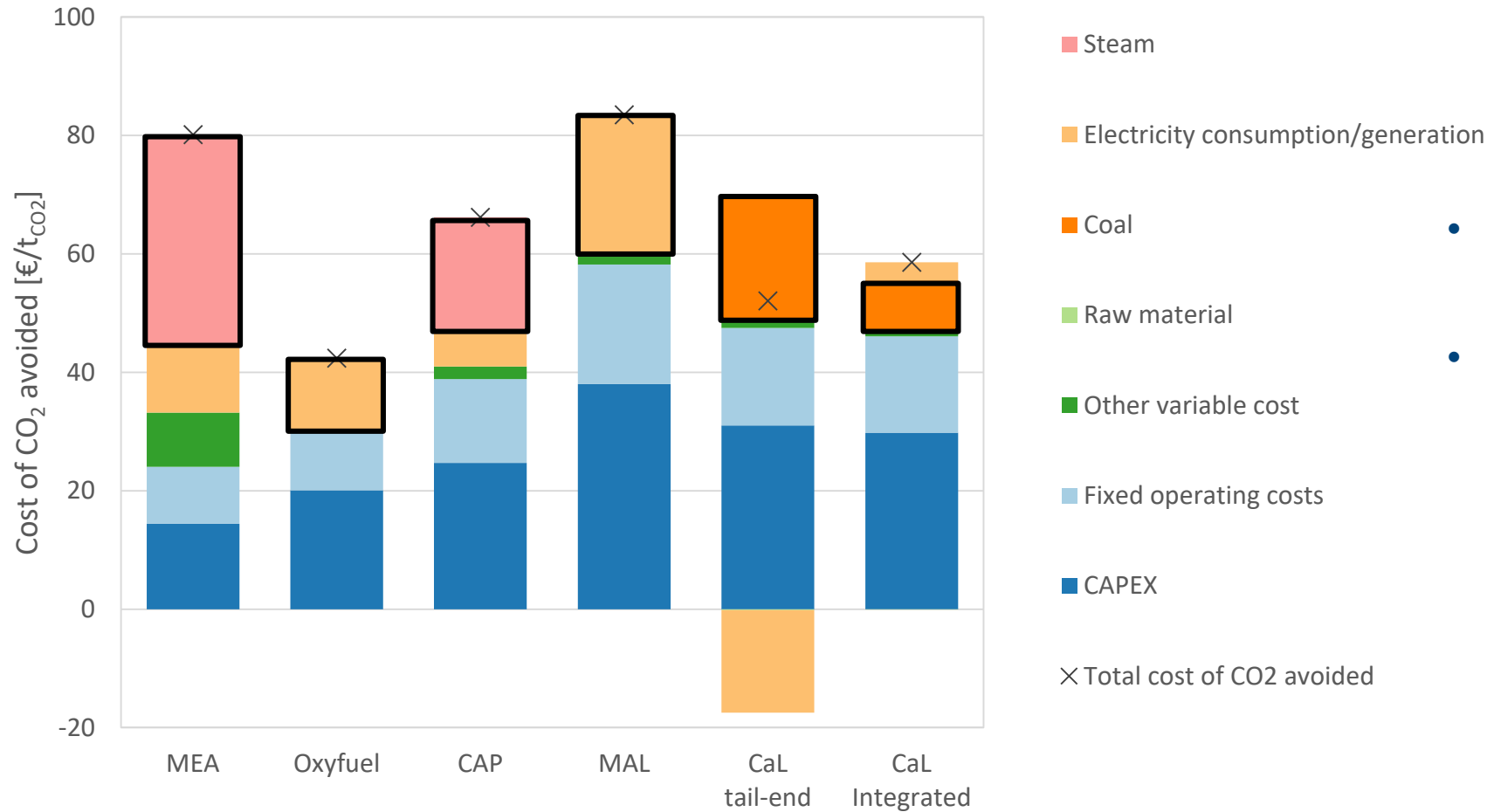
	Post-combustion solvents	Oxyfuel	Calcium looping	Externally heated calcination
Direct CO ₂ emissions				
Direct fuel consumption				
Electricity consumption				
Indirect fuel consumption and CO ₂ emissions				
Capital costs				

Increase rate depends on electric grid mix

Need of steam generation may increase emissions and fuel consumption in the cement kiln battery limit



CEMCAP Benchmarking: cost of CO₂ avoided



- Investment costs: 40-50% of cost share in all the technologies
- Operating costs of CO₂ avoided mainly related to:
 - Increased **electric absorption** for **oxyfuel** and **membrane separation**
 - **Steam demand** for post-combustion **solvent-based separation**
 - Increased **fuel consumption** for **CaL**

Gardarsdottir et al, 2019. Energies 2019, 12, 542.

CEMCAP

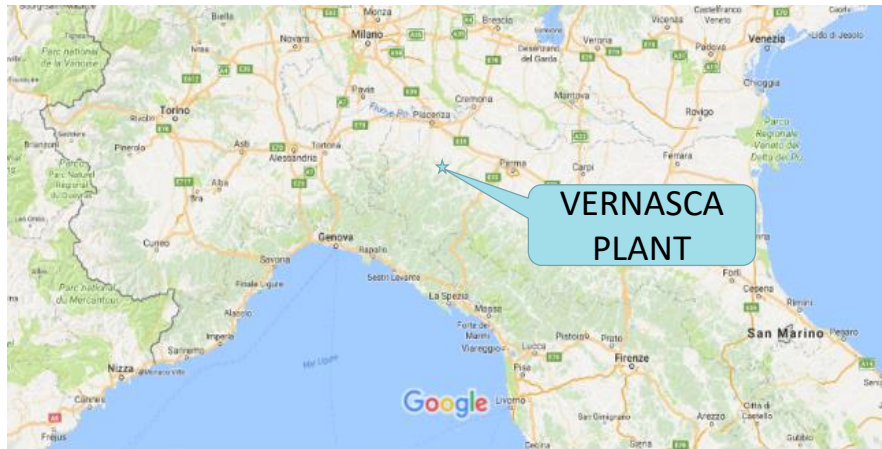


- For cement plants, different CO₂ capture technologies can compete. The optimal technology may be site dependent, as CO₂ avoidance cost depends on: (i) cost of fuel and availability of alternative fuels; (ii) cost of utilities; (iii) needed purity of CO₂; (iv) financial framework, advantaging technologies with partial CO₂ capture and lower investment costs; (v)....?
- Calcium looping is one of the (best) players on the ground!
- ... but for the integrated CaL process, pilot scale demonstration and more accurate scale-up study is needed to answer some research questions



Project objectives

The ultimate objective of CLEANKER is advancing the integrated Calcium-looping process for CO₂ capture in cement plants.



This fundamental objective will be achieved by pursuing the following primary targets:

- Demonstrate the integrated CaL process at TRL 7, in a new demo system connected to the operating cement burning line of the Vernasca 1.300.000 ton/y cement plant, operated by BUZZI in Italy.
- Demonstrate the technical-economic feasibility of the integrated CaL process in retrofitted large scale cement plants through process modelling and scale-up study.
- Demonstrate the storage of the CO₂ captured from the CaL demo system, through mineralization of inorganic material in a pilot reactor of 100 litres to be built in Vernasca, next to the CaL demo system.

The consortium

Starting date: October 1st 2017

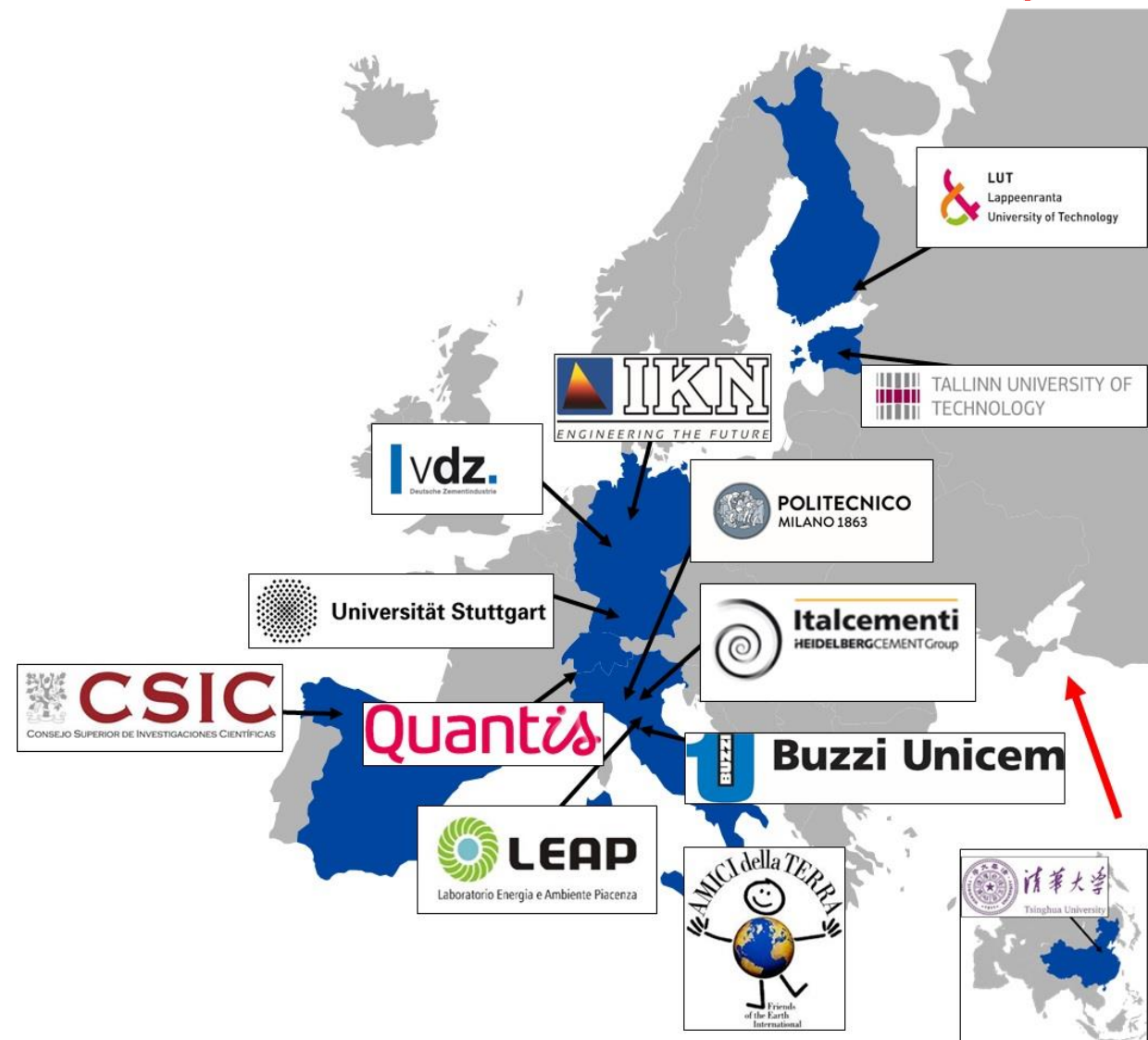
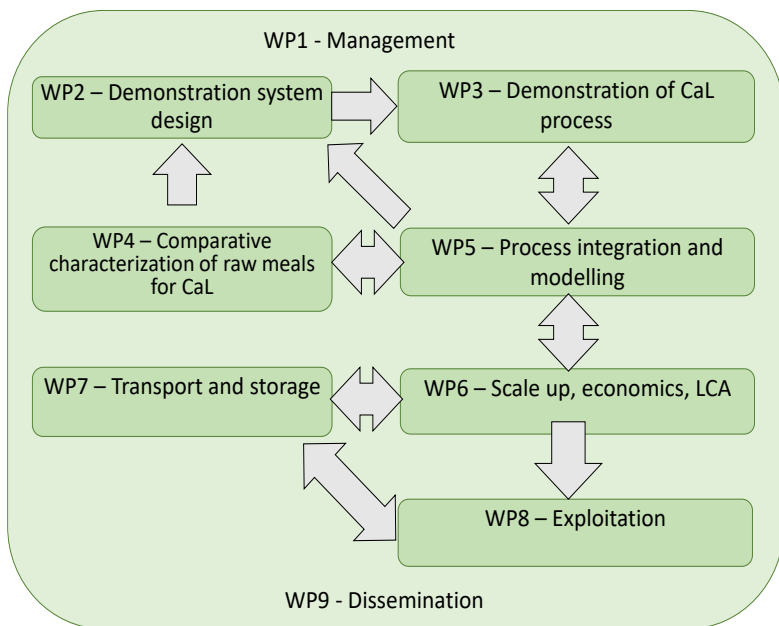
Duration: 4 years

Total budget: € 9.237.851,25

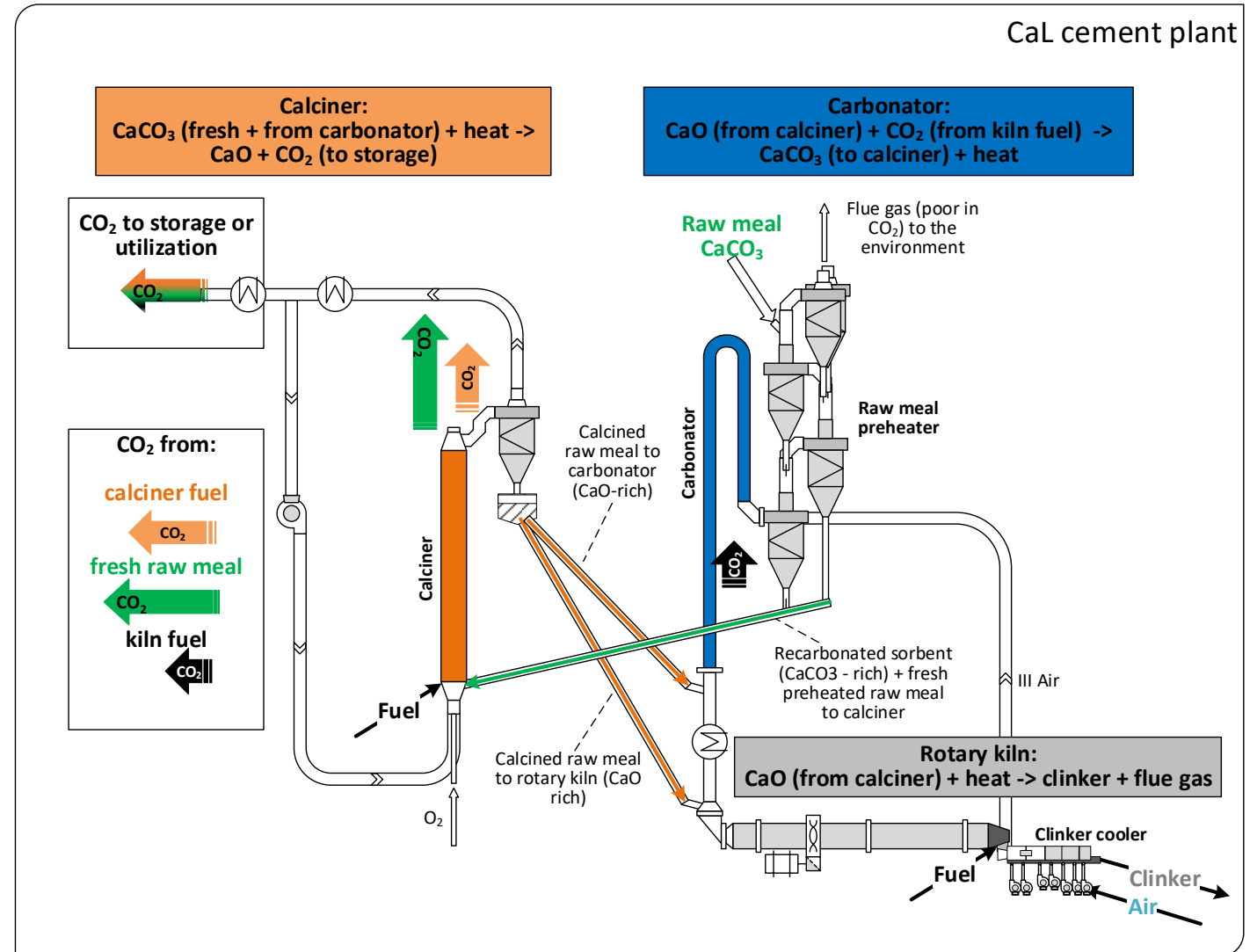
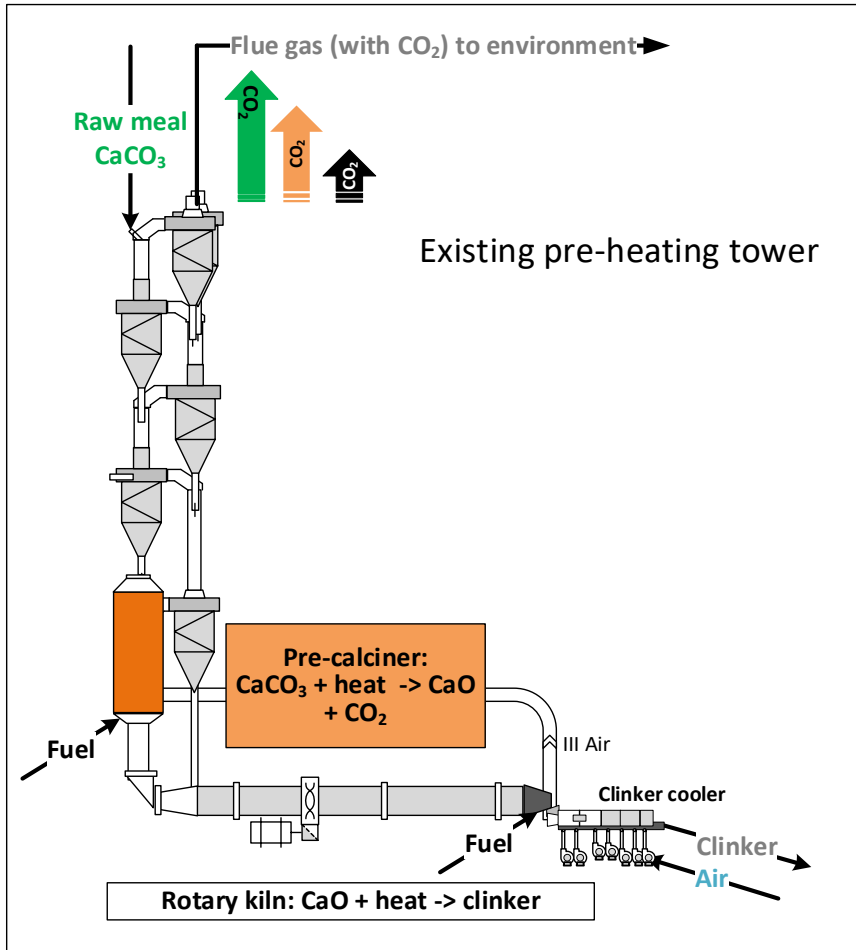
UE co-financing: € 8.972.201,25

Chinese government funding: 265.650 €

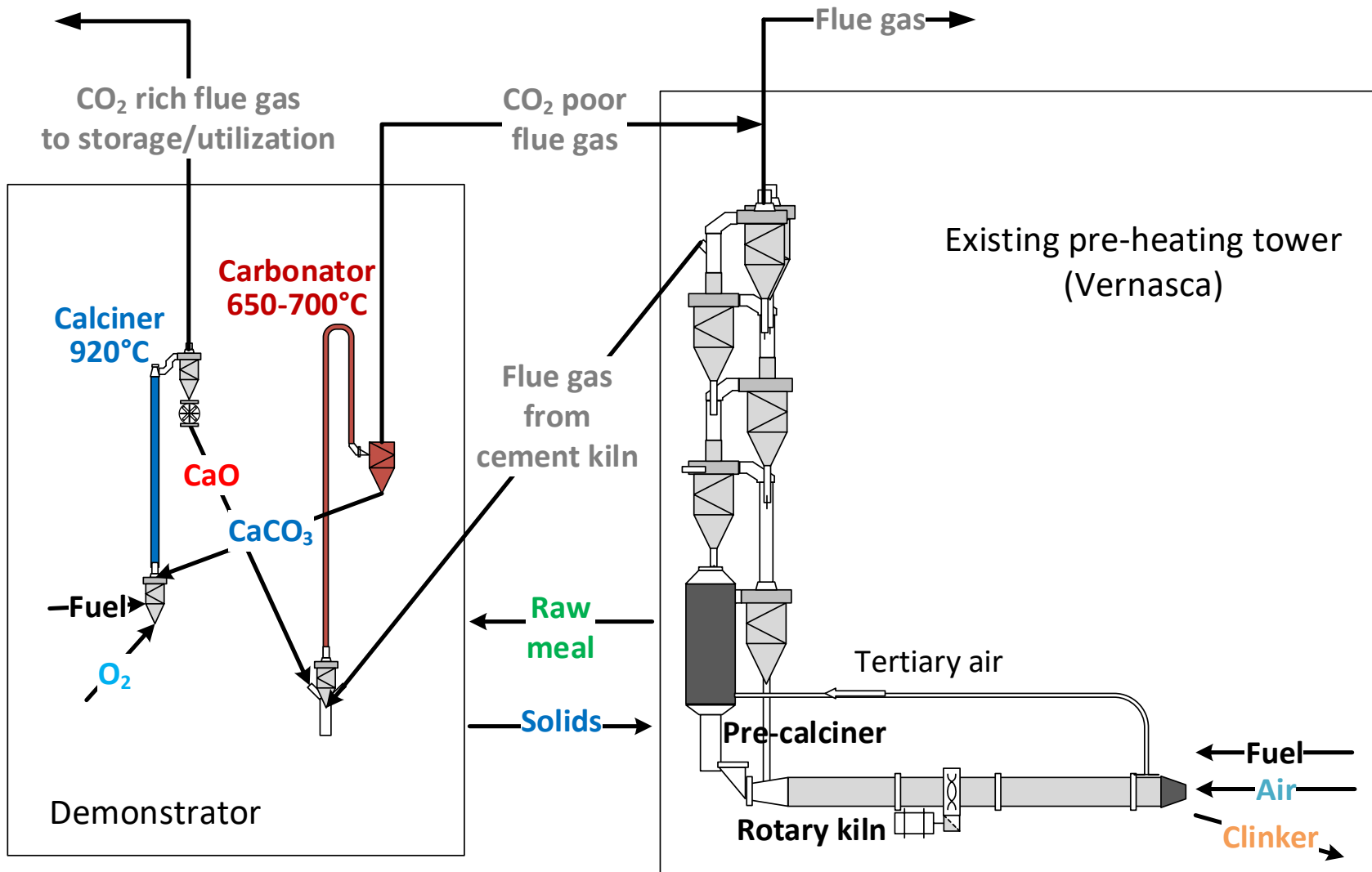
Partner: 13 from 5 EU member states + Switzerland and China



CaL integrated configuration

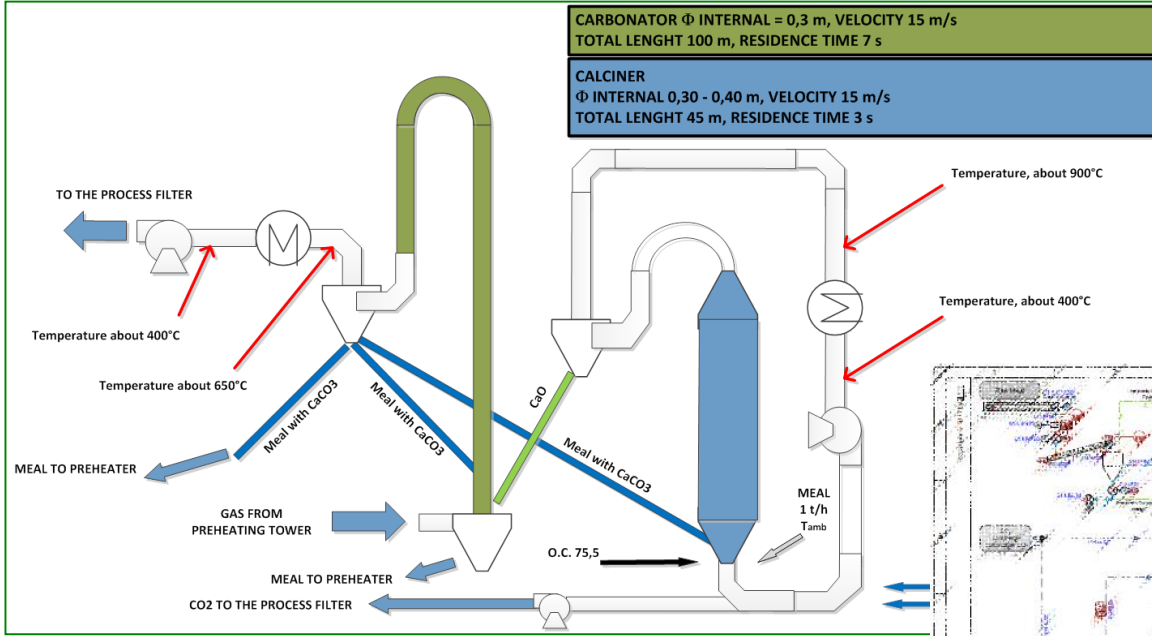


CLEANKER demo system

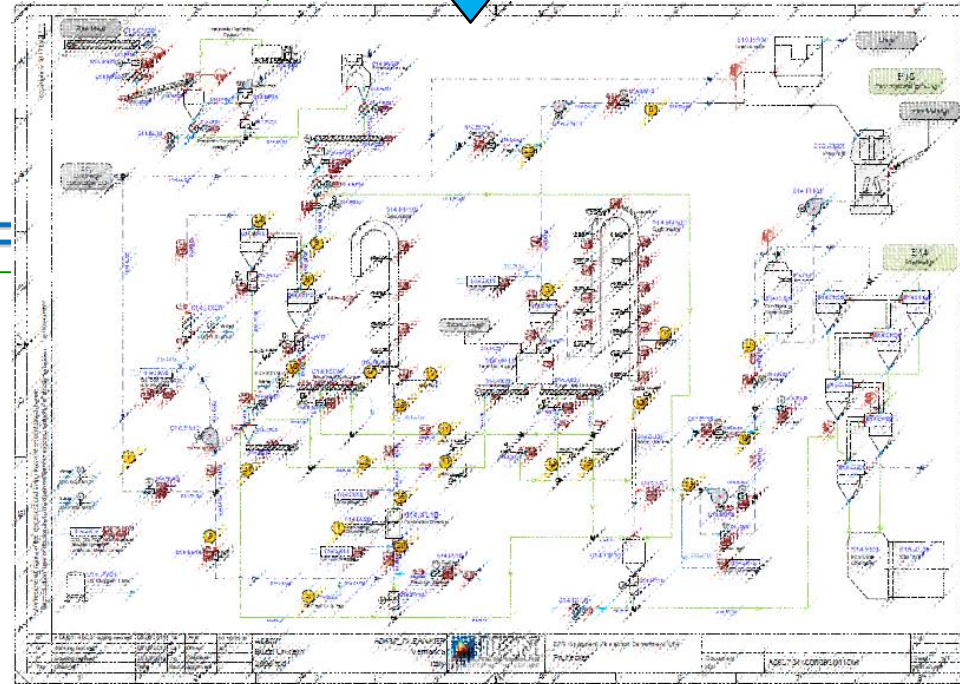


CLEANKER demo system

BASIC FLOWSHEET FOR THE APPLICATION



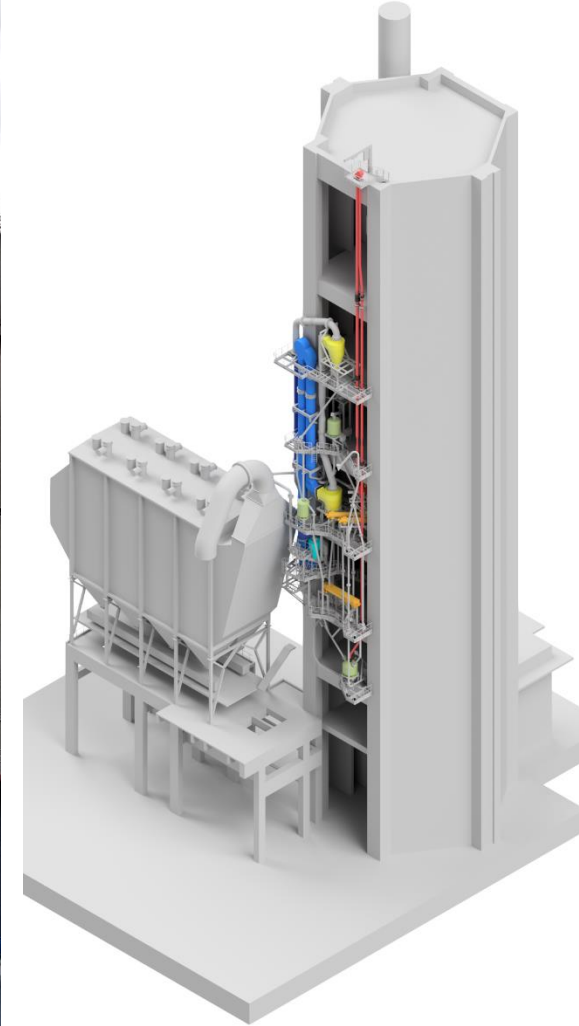
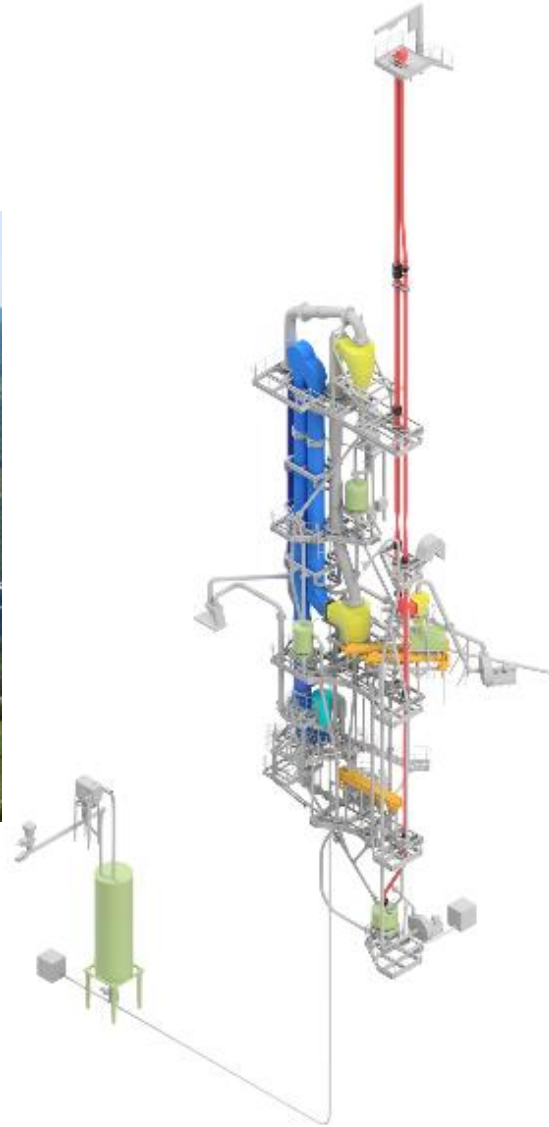
FINAL FLOWSHEET OF THE TEST RIG



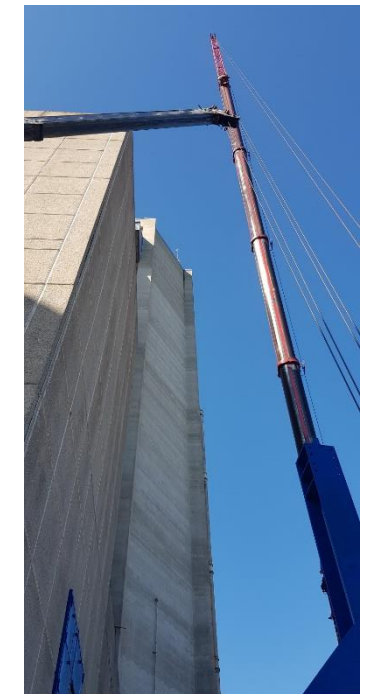
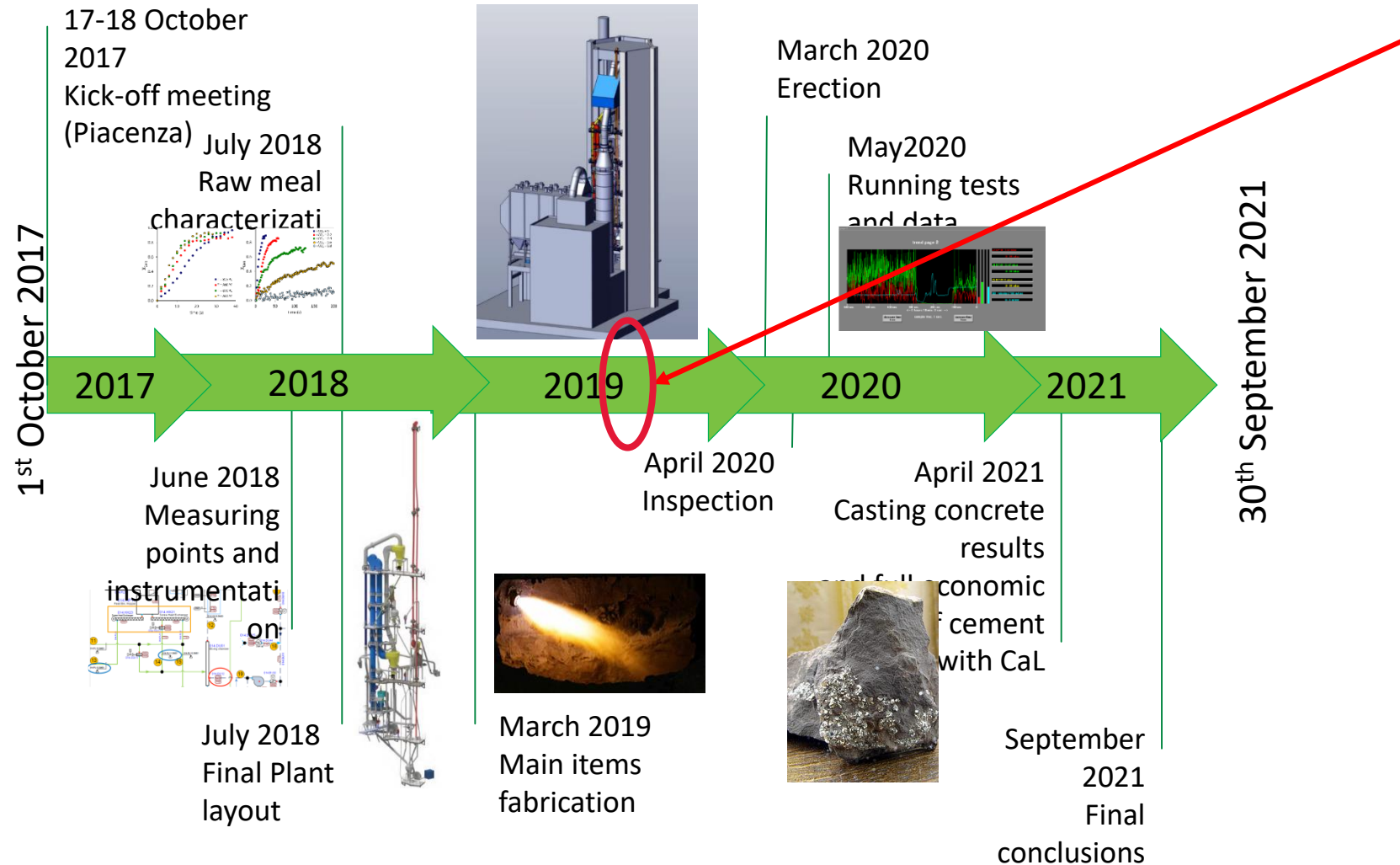
CLEANKER demo system



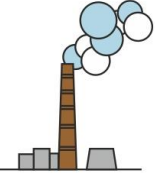


Preheater tower



CLEANKER timeline



CLEANKER targets

Objective	Key indexes	Target
CO₂ emissions 	<ul style="list-style-type: none"> • CO₂ capture efficiency • CO₂ specific emissions 	<ul style="list-style-type: none"> • Cement plant CO₂ capture efficiency >90% • Negative direct CO₂ emissions by biomass co-firing (Bio-CCS) • Reduction of total CO₂ specific emissions (kg_{CO2} per ton of cement) >85%
Energy efficiency 	<ul style="list-style-type: none"> • Fuel consumption • Electricity consumption • Specific primary energy consumption for CO₂ avoided (SPECCA*) 	<ul style="list-style-type: none"> • increase of total fuel consumption with respect to state of the art plants <40% • increase of electric consumption with respect to state of the art plants <20% • SPECCA* < 2 MJ_{LHV} per kg of CO₂ avoided • SPECCA* at least 10% lower than that of benchmark full oxyfuel cement plants
Economics 	<ul style="list-style-type: none"> • Cost of cement • Cost of CO₂ avoided 	<ul style="list-style-type: none"> • Increase of cement cost < 25 €/t_{cement} • Cost of CO₂ avoided <30 €/t_{CO2}

*SPECCA = Specific primary energy consumption for CO₂ avoided

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