Cleanker pilot test results

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Summary

- *Experimental campaigns*
- *Process Flow Diagram and key parameters investigated*

- *Instrumentation and solid samples analysis*
- *Data analysis method*

- *Limitations of the pilot plant*

- *Results*
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    - *Carbonator operation*
    - *Impact of temperature on CO_2 capture efficiency*
    - *CO_2 purity at calciner outlet*
    - *Calcination degree*

Experimental campaigns

- **9 experimental campaigns**:
  - **5 short tests**: one week each, test of several operating points
  - The aim of the short tests is **to identify the most attractive operating conditions** for the longer test runs
  - **4 long tests**: one week of continuous operation each, test of the most interesting operating conditions for longer periods

- The commissioning started on September 2020
- Short tests: March 2022 to August 2022
- Long tests: November 2022 to February 2023

	Hours (*)
Main burner (fuel oil combustion)	1’180
Calciner (raw meal fed to the calciner)	277
Carbonator (calcined raw meal fed to the carbonator)	214
Full oxyfuel calcination (exclusive use of oxygen as comburent in the calciner)	141

(*) Counter started on 9/11/2021, when the new fuel oil was available. The commissioning started on 28/9/2020

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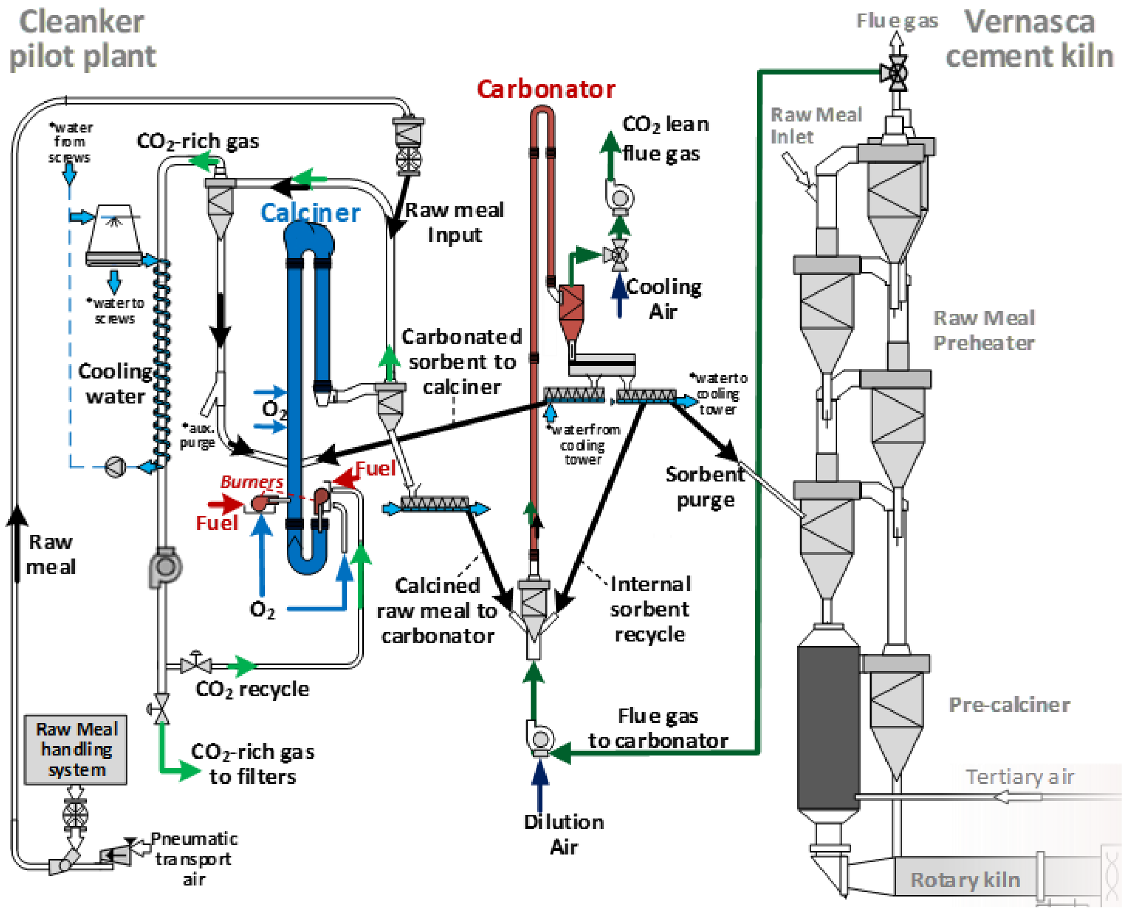
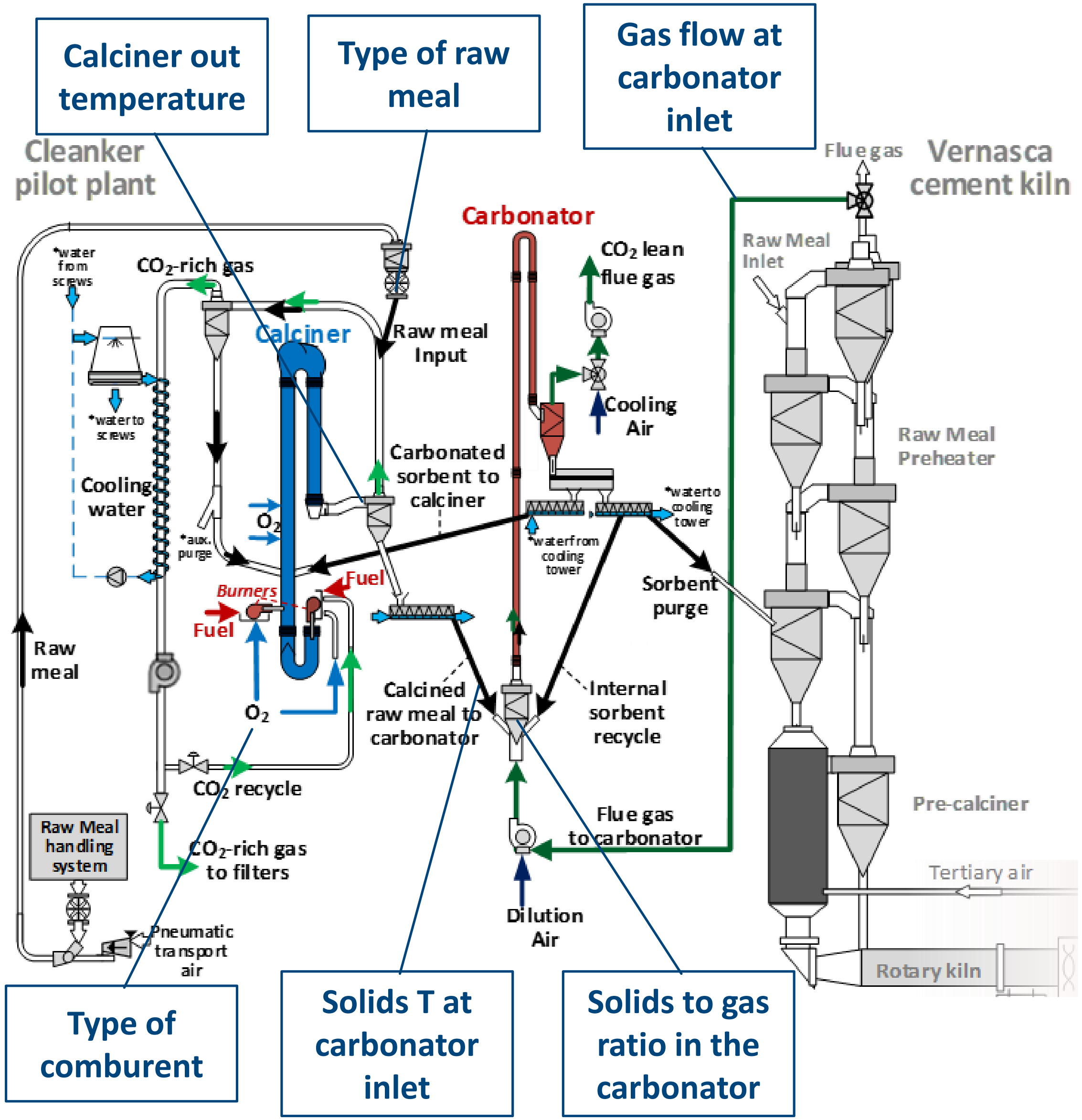
Process Flow Diagram



- **Fresh raw meal** fed to the calciner after 1 preheating stage
- **Combustion system**: 2 oxyfuel burners + 3 additional oxygen injection points
- **CO_2-rich gas recycle** for gas speed and temperature management in the calciner
- **All the calcined material fed to the carbonator**, where it is put in contact with Vernasca preheater tower gas
- **Carbonated material recycled** back to the **calciner** by a screw conveyor, excess material discharged to Vernasca preheater tower

Key parameters investigated



- **Solid to gas ratio in the carbonator** – Available sorbent per kg of CO_2
- **Gas flow rate at carbonator inlet** – Residence time
- **Solids temperature at carbonator inlet** – Thermodynamics and kinetics of carbonation
- **Air-fired/oxyfuel calcination**
- **Calciner outlet temperature** – Calcination degree
- **Type of raw meal**

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Instrumentation

- **Continuous measurements:**
  - **Gas composition:** carbonator inlet and outlet, calciner inlet (recycle)
  - **Temperature and pressure:** 36 thermocouples + 28 pressure transducers
    in particular, every 10 m on carbonator and calciner to get complete profiles
  - **Gas flow rate:** Venturis on carbonator (2) and calciner outlet (1) + estimate from fan characteristic curve for the carbonator
  - **Combustion:** total fuel flow (heavy fuel oil), total O_2 flow, primary air flow
  - **Feedback from machinery and other sensors:** rotating speed, absorbed current/power, position of valves and slide gates, status of level switches…
- **All the signals are available in the control room and recorded for successive analysis**

- **Discontinuous (manual) measurements:**
  - **Solid sampling:**
    - Raw meal, typically sampled once per week
    - Calciner and carbonator outlet, every 1-2 h
    - Other ports long the carbonator, during dedicated tests only

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Solid samples analysis

- **Type of analysis:**
  - **Loss On Ignition (LOI)**
    - Performed directly in Vernasca: quick analysis, useful for the operation, performed on all the samples from both short and long tests

    → Amount of CO_2 bound to the sample
  - **Thermogravimetric Analysis (TGA)**
    - Performed by University of Stuttgart and CSIC, on all samples from short test + selected samples from long tests

    → Actual and maximum achievable recarbonation
  - **X-ray Diffraction (XRD)**
    - Performed by VDZ on selected samples from both short and long tests

    → Mineralogical phases (e.g. belite formation)
  - **X-ray Fluorescence spectroscopy (XRF)**
    - Performed by VDZ on selected samples from both short and long tests

    → Chemical composition

Data analysis method

- **Data collection:**
  - **All the data available for a test week** (both continuos and discontinuous) **in a single file** with 1-minute average values
  - **Small corrections** to take into account delay in some measurements (e.g. gas analysis due to sampling line) and **minor data cleaning** (e.g. removing clearly unreasonable points)

- **Calculation** of **derived operating parameters** (e.g. solid-to-gas ratios) and **main KPIs** (e.g. carbonator capture efficiency)

- **Definition of the experimental points**, based on:
  - **Availability of solid samples**
  - **Stability** (few minutes for short test, as long as possible for long tests)

- **Simulation of the most interesting experimental points on Aspen Plus** (heat and mass balances)

  → Data provided to other project Work Packages for **model validation and tuning**

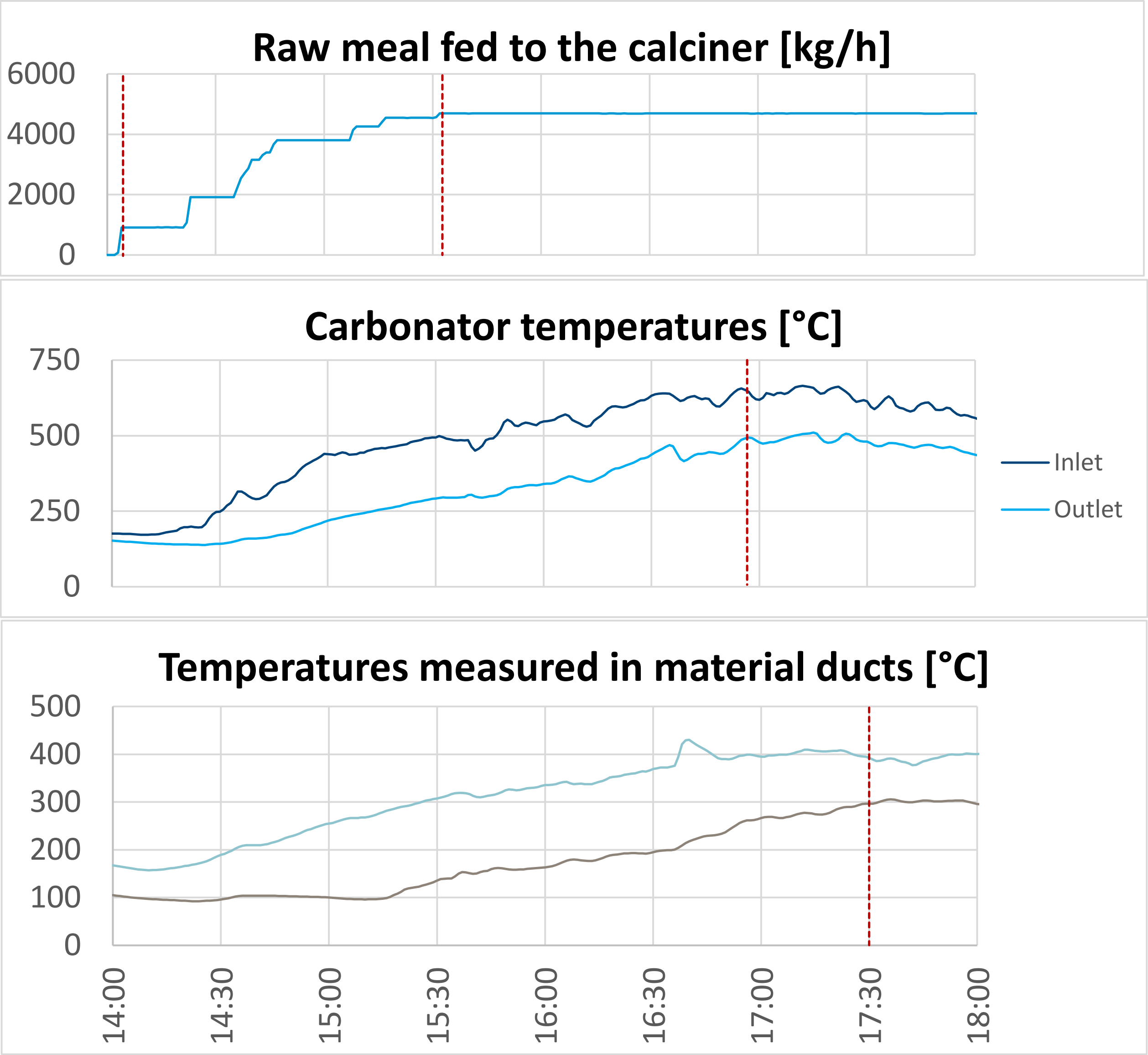
Limitations of the pilot plant

- **Frequent clogging** due to the small size of discharge lines
- **Extremely interconnected system**
  - → Undesired flows
  - → Difficulty in identifying the source of several issues
- **Low inertia of the carbonation section**
  - → Unstable measurements
- **Use of a (too) heavy fuel oil** at the beginning
- **Complexity of the system**
  - → Anomalies of 'secondary' machines repeatedly forced to stop the experiments
- **Demanding maintenance operations required between the tests**

- **Inherent difficulty in measuring solids temperature**
- **False air ingress**

- **However, these issues are mainly related to the small scale of the pilot**
  - → Bigger scales should help in limiting them

Results – System stability



- **Typical time to get to system equilibrium**
- Data from Long Test #4, 22/2/2023, h 14,00 – 18,00

- 14:00 Start of material feeding
- 15:30 Target material feed reached
- 17:00 Carbonator equilibrium reached
- 17:30 Full equilibrium reached

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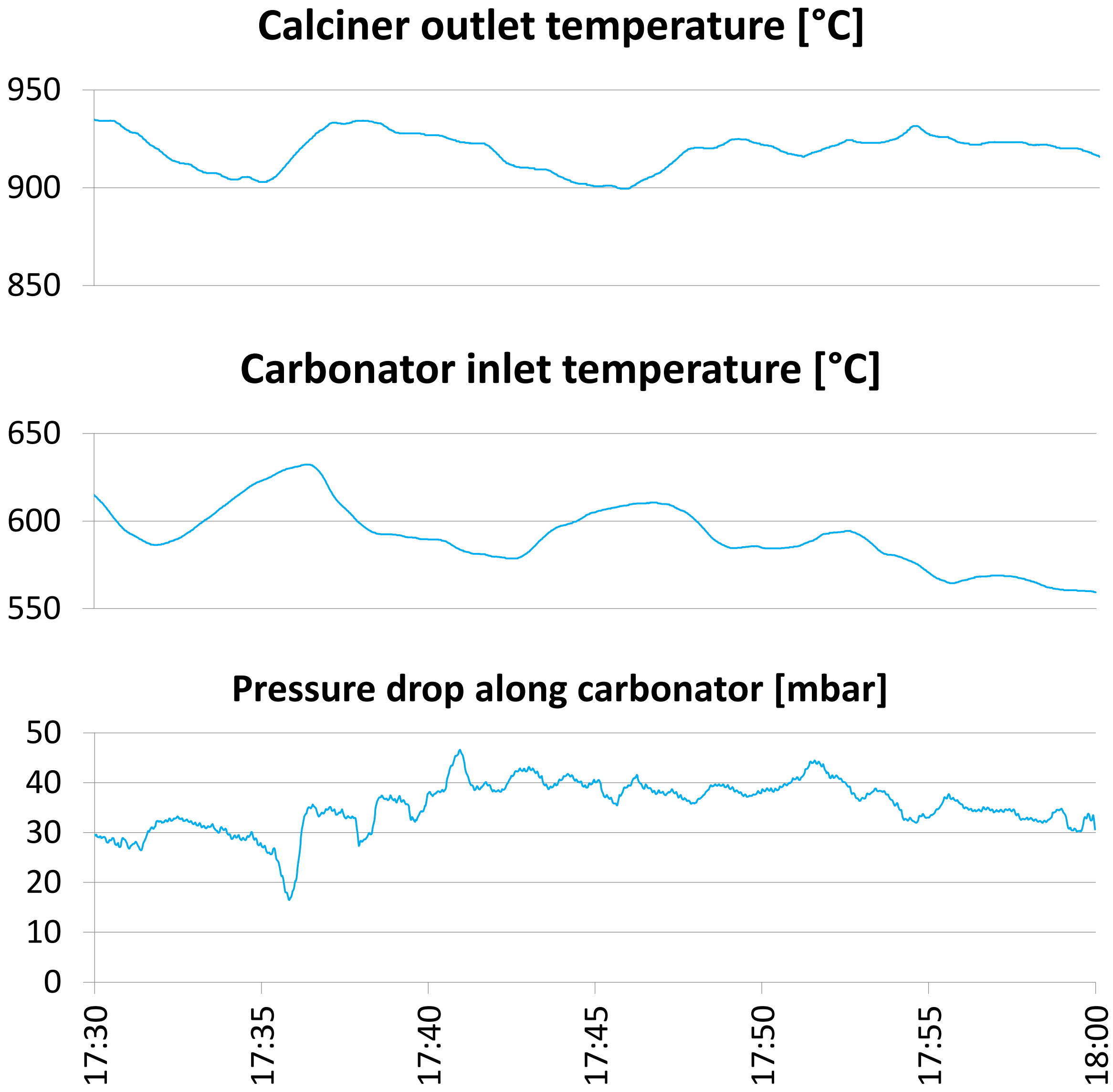
Results – System stability



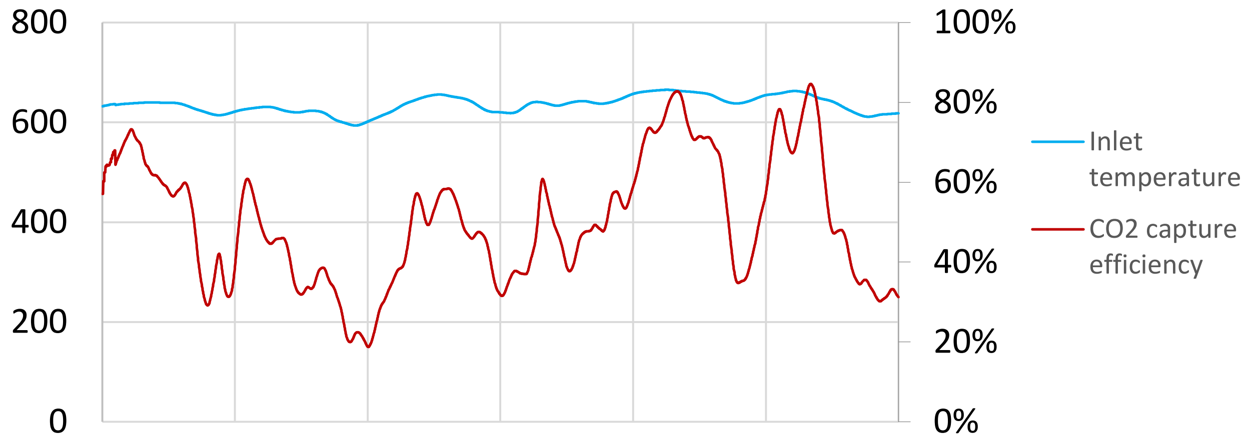
- **System stability when full equilibrium is reached**
- Data from Long Test #4, 22/2/2023, h 17,30 – 18,00

Solids fed to the calciner	
Fresh raw meal, kg/h	2’550
Carbonated raw meal, kg/h	2’150
Calciner outlet	
Average temperature, °C	919
CO_2 purity, $\%_{dry}$	53,3

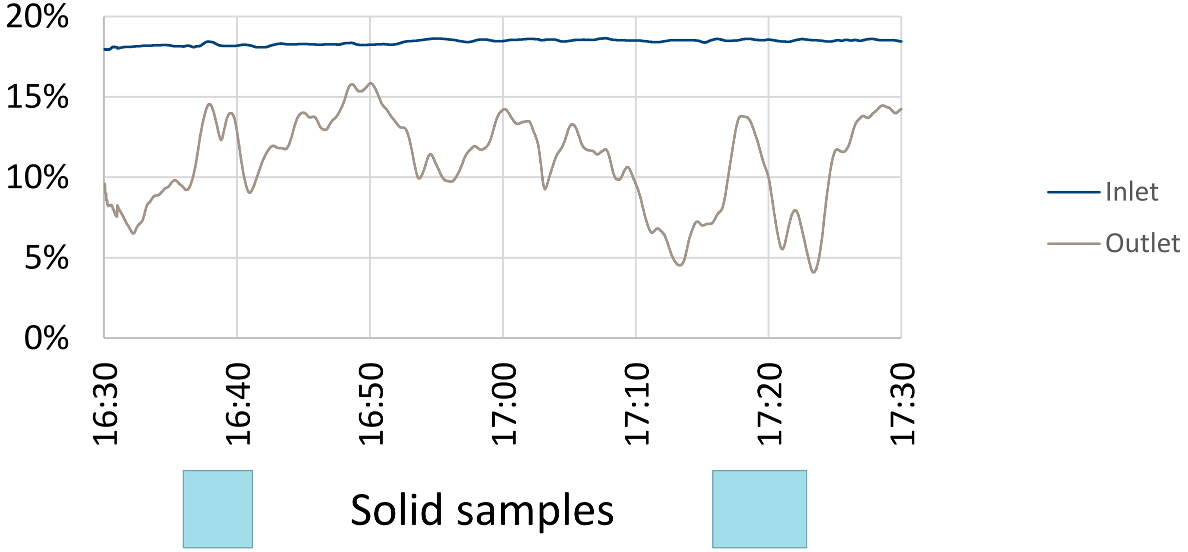
- Even if the **operating conditions** are kept **constant** and **full equilibrium** is reached (as defined before), the **oscillations in the carbonator are not negligible**
- *NB: «Carbonator inlet temperature» is the temperature measured by the first thermocouple inside the carbonator (**solid-gas mixture**)*

Results – Carbonator operation

Carbonator inlet temperature [°C] and CO_2 capture efficiency [%]



CO_2 concentration at carbonator inlet/outlet [%dry @10% O_2]



- Data from Long Test #4, 22/2/2023, h 16,30 – 17,30

Solids fed to the calciner	
Fresh raw meal, kg/h	2’550
Carbonated raw meal, kg/h	2’150
Calciner outlet	
Average temperature, °C	915
CO_2 purity, $\%_{dry}$	52,2

- Material feed and calcination conditions are kept constant → **carbonator inlet temperature is the main parameter affecting CO_2 capture**
- CO_2 capture is visible from CO_2 concentrations at carbonator inlet/outlet (reported @10% O_2)

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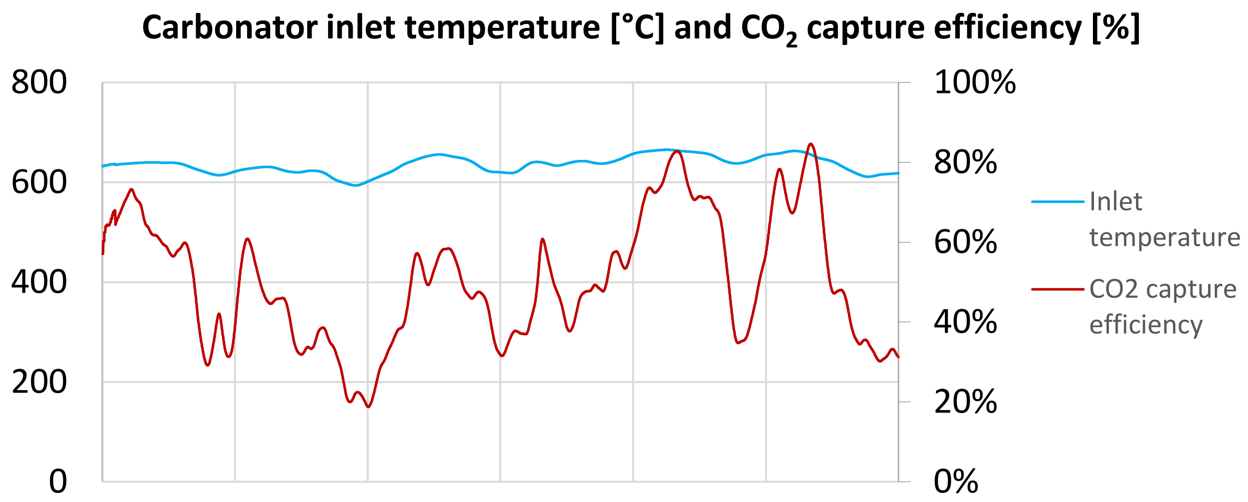
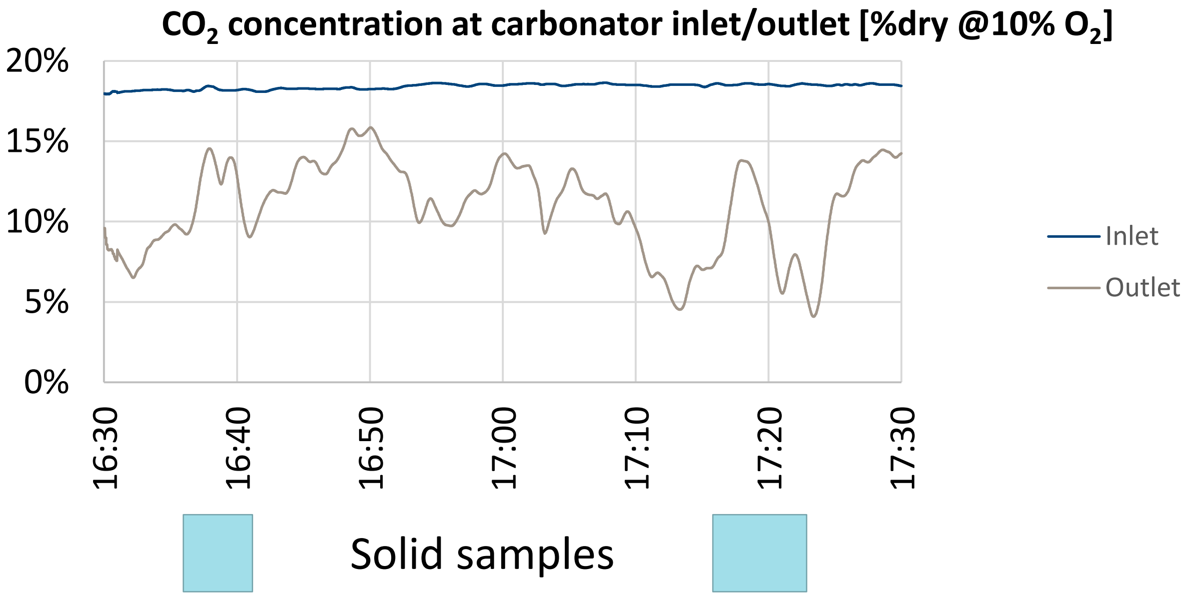
Results – Carbonator operation





- Data from Long Test #4, 22/2/2023, h 16,30 – 17,30

Sampling time	16,36 – 16,41	17,16 – 17,23
Temperatures		
Calciner outlet, °C	911	918
Carbonator inlet, °C	624	651
Carbonator average, °C	527	568
TGA results		
Actual carbonation degree (Xcarb)	0,327	0,324
Maximum carbonation degree (Xmax)	0,449	0,433
Xcarb/Xmax	72,8 %	74,8 %

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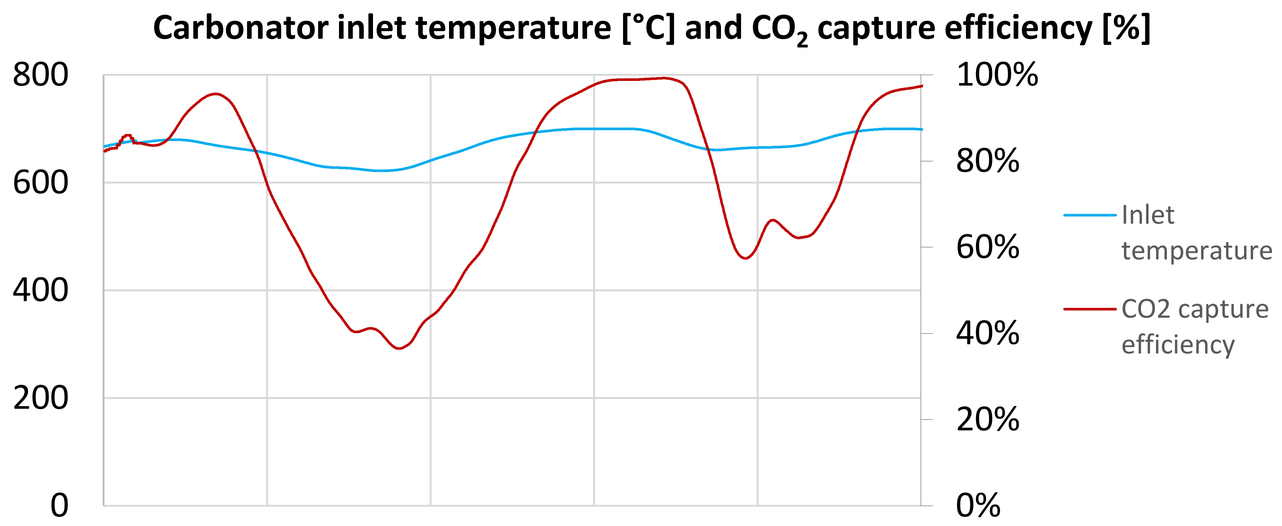
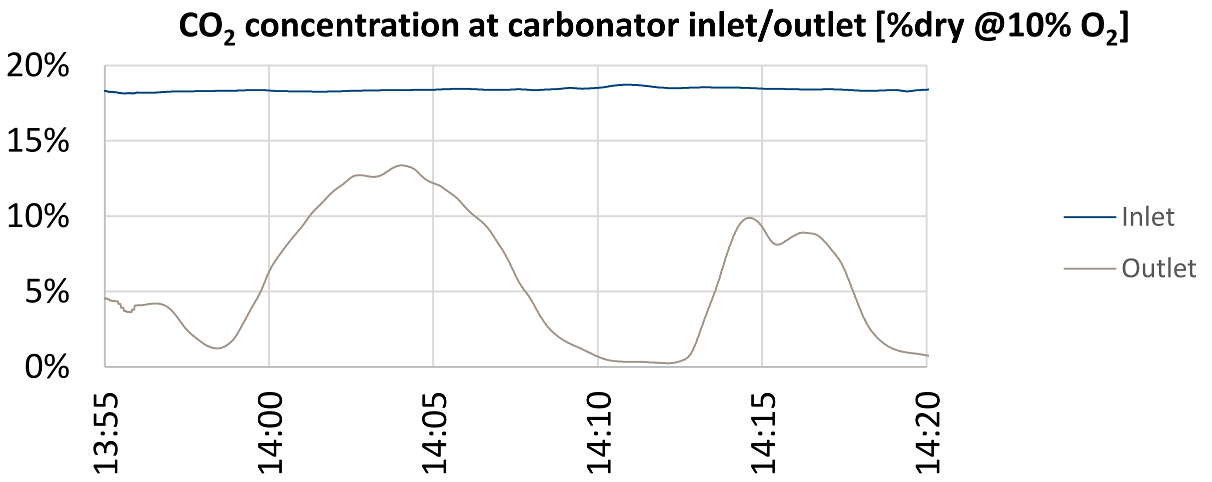
Results – Carbonator operation





Solid sample | 14,06 – 14,17

- Data from Long Test #4, 23/2/2023, h 13,55 – 14,20

Solids fed to the calciner	
Fresh raw meal, kg/h	2’900
Carbonated raw meal, kg/h	2’500
Calciner outlet	
Average temperature, °C	899
CO_2 purity, $\%_{dry}$	49,7

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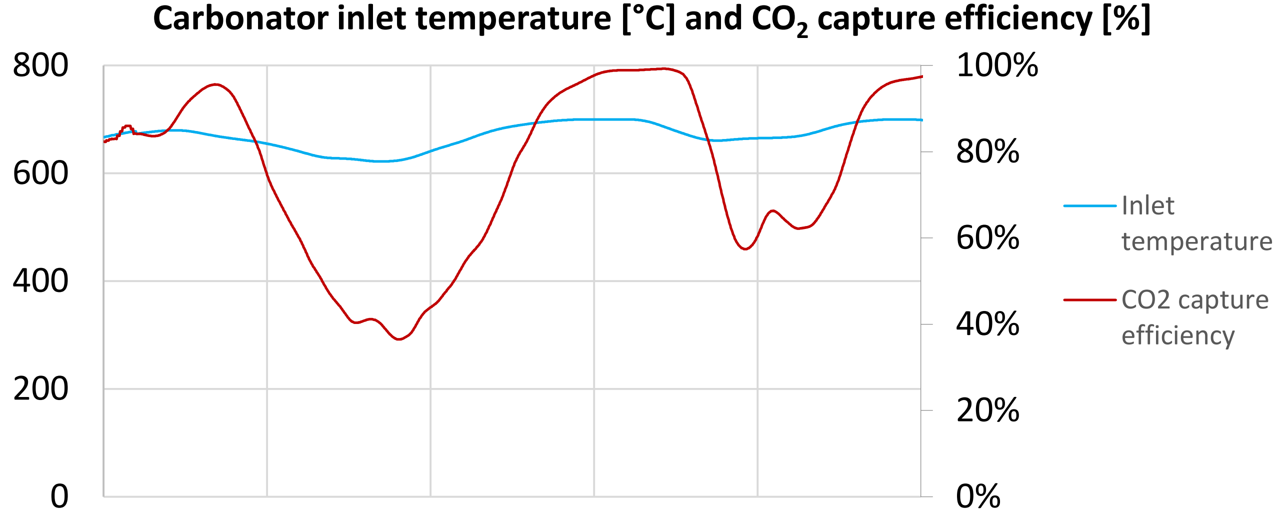
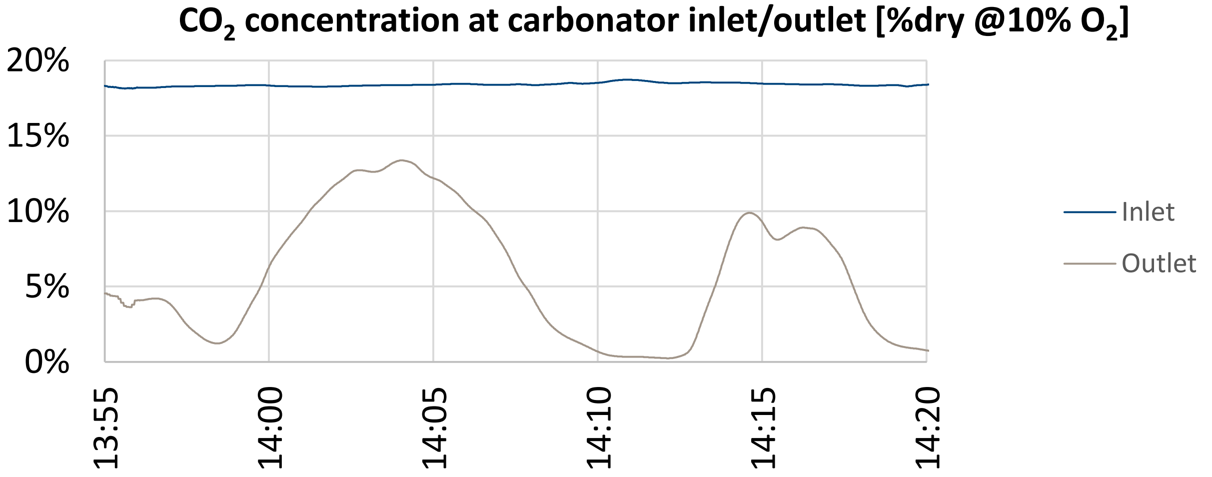
Results – Carbonator operation



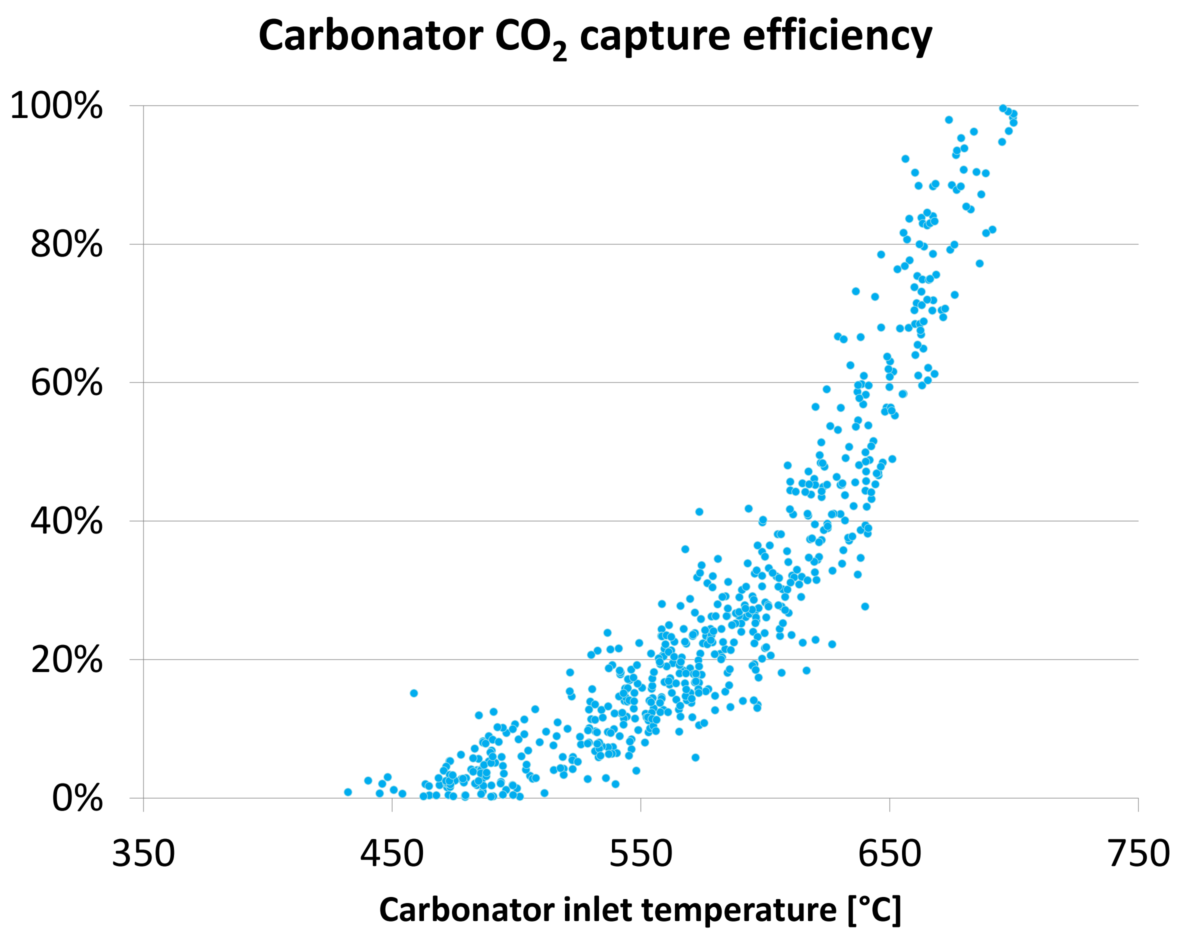


Solid sample | 14,06 – 14,17

- Data from Long Test #4, 23/2/2023, h 13,55 – 14,20

Sampling time	14,06 – 14,17
Temperatures	
Calciner outlet, °C	893
Carbonator inlet, °C	682
Carbonator average, °C	627
TGA results	
Actual carbonation degree (Xcarb)	0,280
Maximum carbonation degree (Xmax)	0,367
Xcarb/Xmax	76,3 %

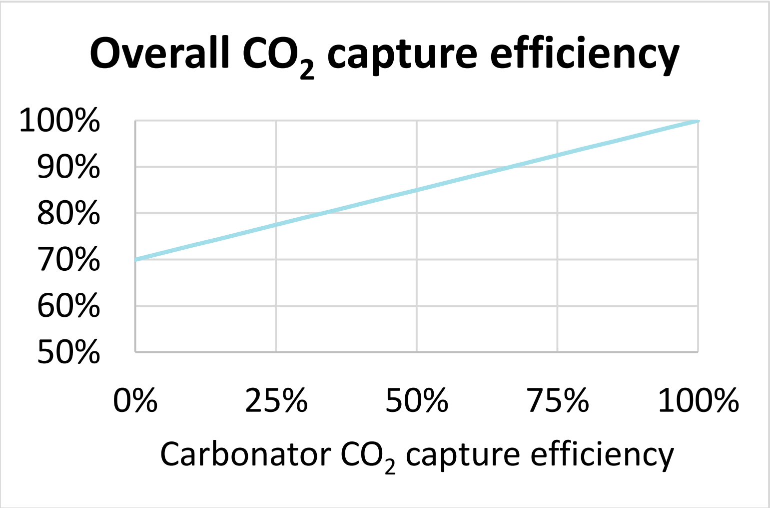
Results – Impact of temperature on CO_2 capture efficiency



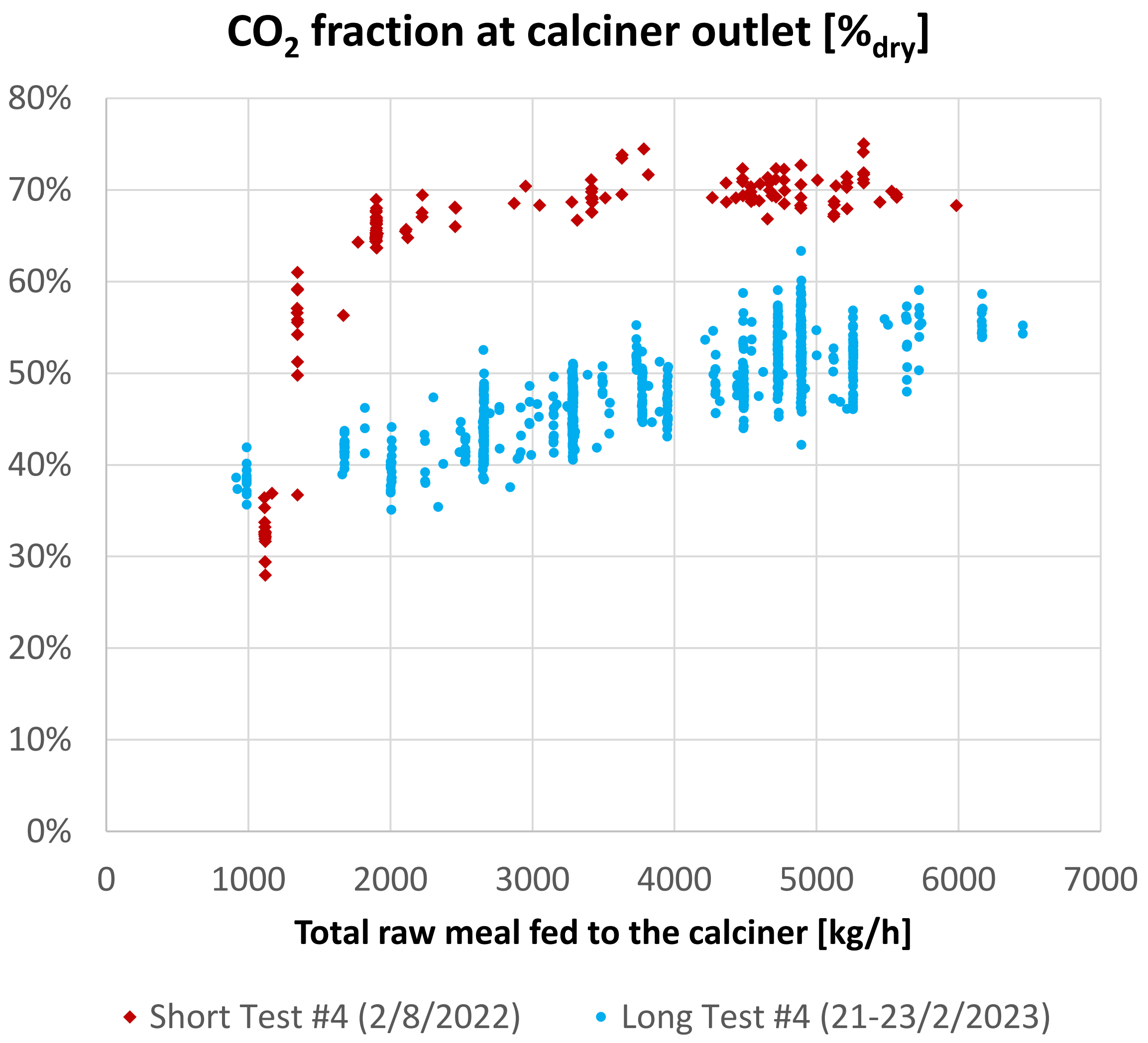
- **Carbonator CO_2 capture efficiency vs Temperature**
- Data from Long Test #4, 22-23/2/2023

- **The correlation between carbonator CO_2 capture efficiency and temperature is clearly visible**

- *NB: assuming e.g. 70% of the CO_2 is produced in the oxyfuel calciner, a **carbonator CO_2 capture efficiency of 67%** reflects on a **90% overall CO_2 capture efficiency***



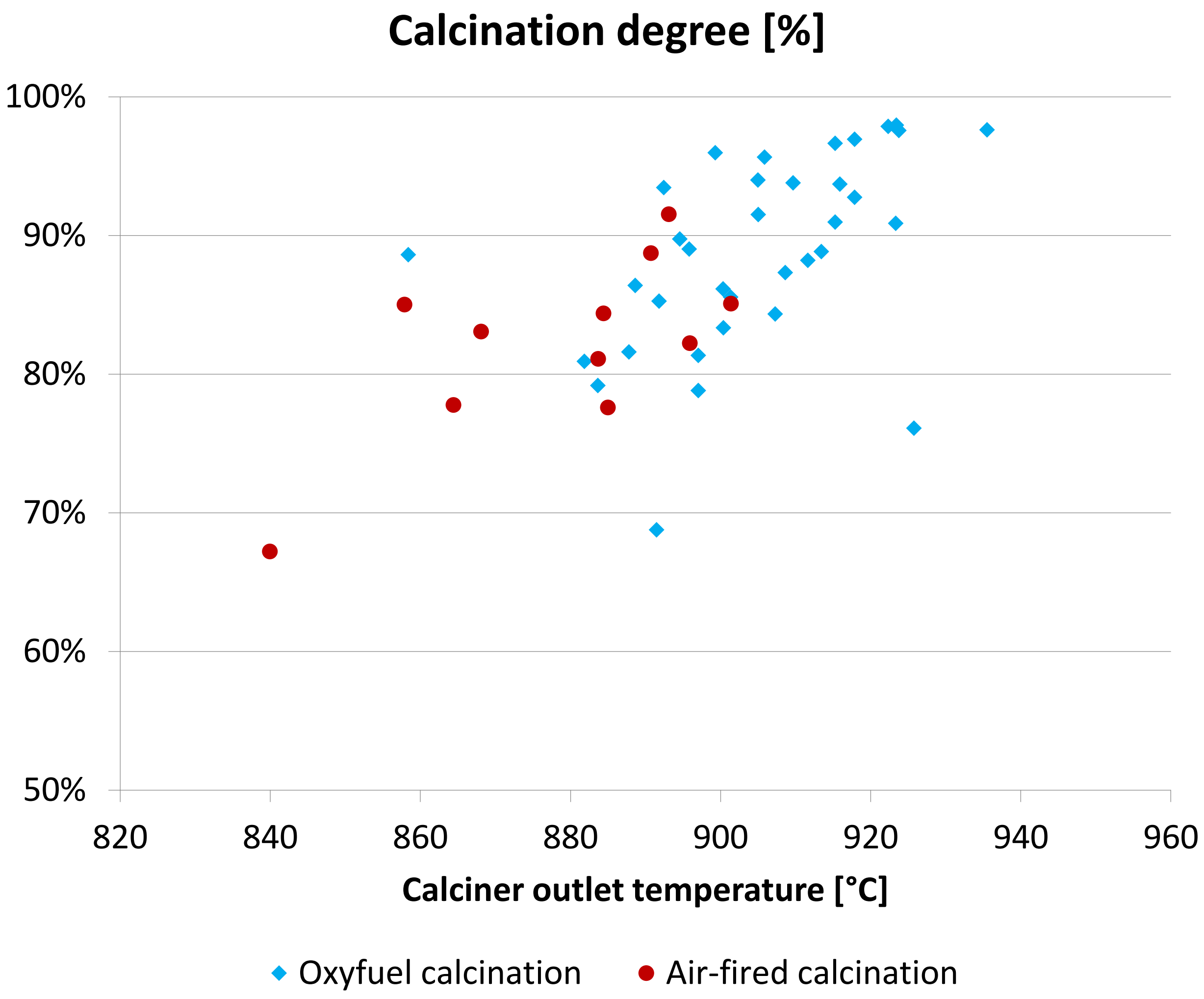
Results – CO_2 purity at calciner outlet



- **CO_2 purity at calciner outlet** vs **total raw meal fed to the calciner** (fresh raw meal + carbonated raw meal)
- Data from:
  - Short Test #4, 2/8/2022
  - Long Test #4, 21-23/2/2023

- **The purity of the CO_2 leaving the calciner is clearly linked to the total amount of material fed to the calciner itself**
- When total amount of material fed to the calciner ↑:
  - CO_2 from fresh raw meal calcination ↑
  - CO_2 from carbonated raw meal (re)calcination ↑
  - Calciner outlet temperature =, CO_2 from fuel ↑
  - False air ingress =
- **False air ingress** likely **increased during the 6 months** between Short Test #4 and Long Test #4

Results – Calcination degree



- **Calcination degree vs Temperature**
- **Air-fired vs oxyfuel conditions**
- Data from:
  - Preliminary tests and Short Test #1, 9-30/3/2022, for air-fired calcination
  - Long Tests #1-4, 8/11/2022 – 23/2/2023, for oxyfuel calcination

- The **correlation** between calcination degree and calciner outlet temperature is **visible** and **comparable to industrial experience**
- **The trends look similar for air-fired and oxyfuel calcination**

Conclusions

- The **raw meal actually used to produce clinker is subject to recarbonation**, not only under laboratory conditions but also **under real operating conditions**. Hence, raw meal **can be actually used as a sorbent for CO_2 capture**
- The uncertainties related to material properties and to the formation of undesired species are overcome

- Analysis on both gas and solid samples indicate **good capture performance in the 500-700 °C range**
- **Increasing the amount of CaO improves the carbonator capture efficiency**

- **Oxyfuel calcination operation is stable and reliable**
- **The purity of the produced CO_2 exceeded 70%** (in a small scale pilot plant)

- **The main issues** which slowed down the experimental activity **are related to the small size of the pilot plant** itself, hence they should be significantly limited at bigger scales

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Acknowledgments

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  - The partners coming to Vernasca
  - The personnel of Vernasca facility
  - The team carrying out the experiments

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