CLEAN clinKER by calcium looping for low-CO_2 cement

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Characterization of cement raw meal as CO_2 sorbent in an entrained flow calcium looping CO_2 capture system for cement plants

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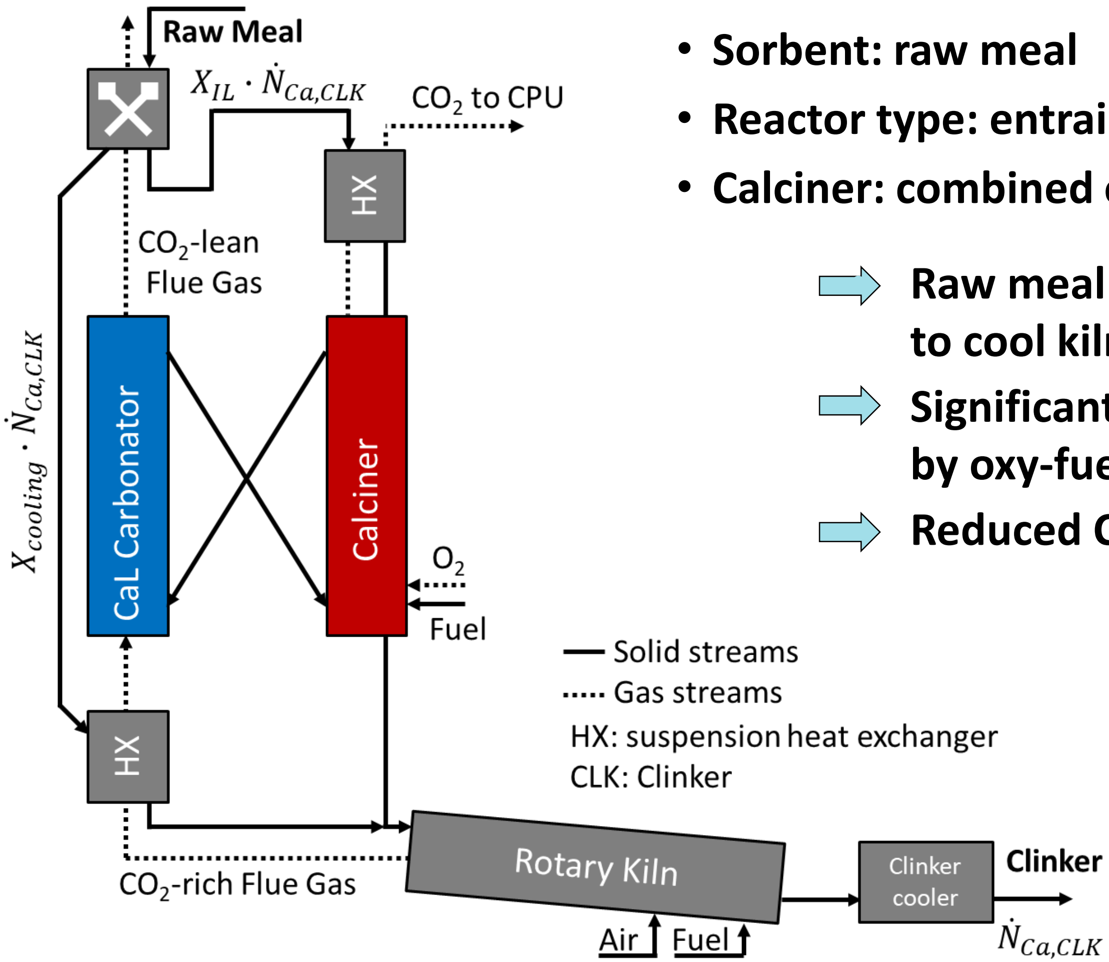
Entrained flow CaL CO_2 capture from cement plants



CaL characteristics:

- **Sorbent: raw meal**
- **Reactor type: entrained flow (EF)**
- **Calciner: combined oxy-fuel calciner**

➡ **Raw meal split stream required to cool kiln off gas**

➡ **Significant share of CO_2 capture by oxy-fuel calcination**

➡ **Reduced CO_2 loading of flue gas**

WP4: Comparative characterization of raw meals for CaL

Main activities

- Determination of calcination and carbonation conversion and kinetics of various raw meal qualities representative for Europe

Main results:

- ⇨ Extrapolation of the Calcium Looping demonstration test in Vernasca to other cement plants/raw meal qualities
- ⇨ Development of a guideline on raw meal characterization in respect to suitability for Calcium Looping applications

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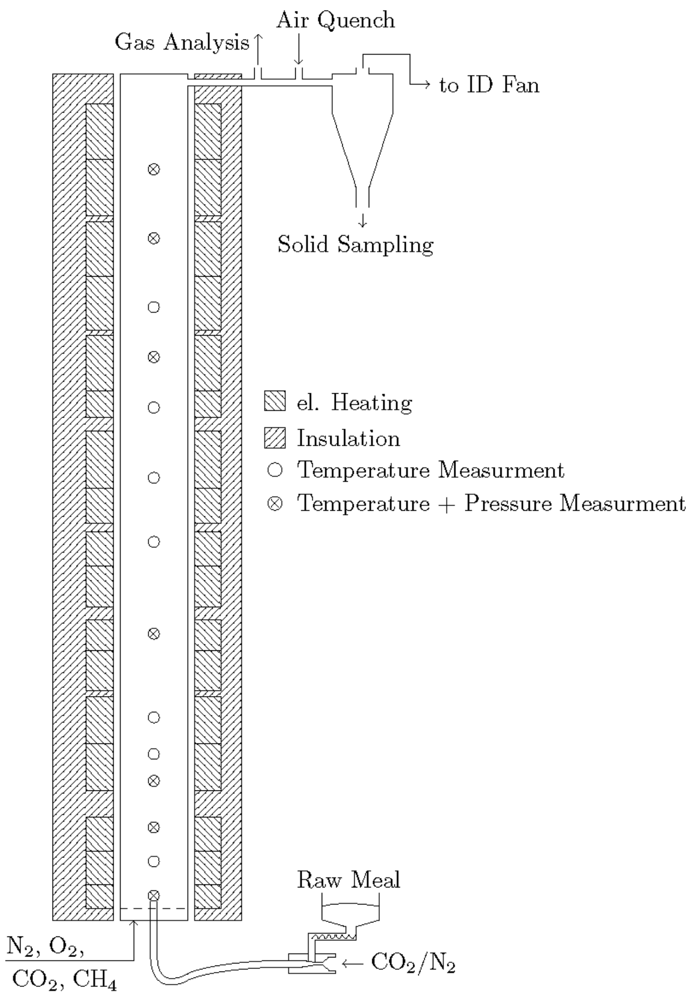
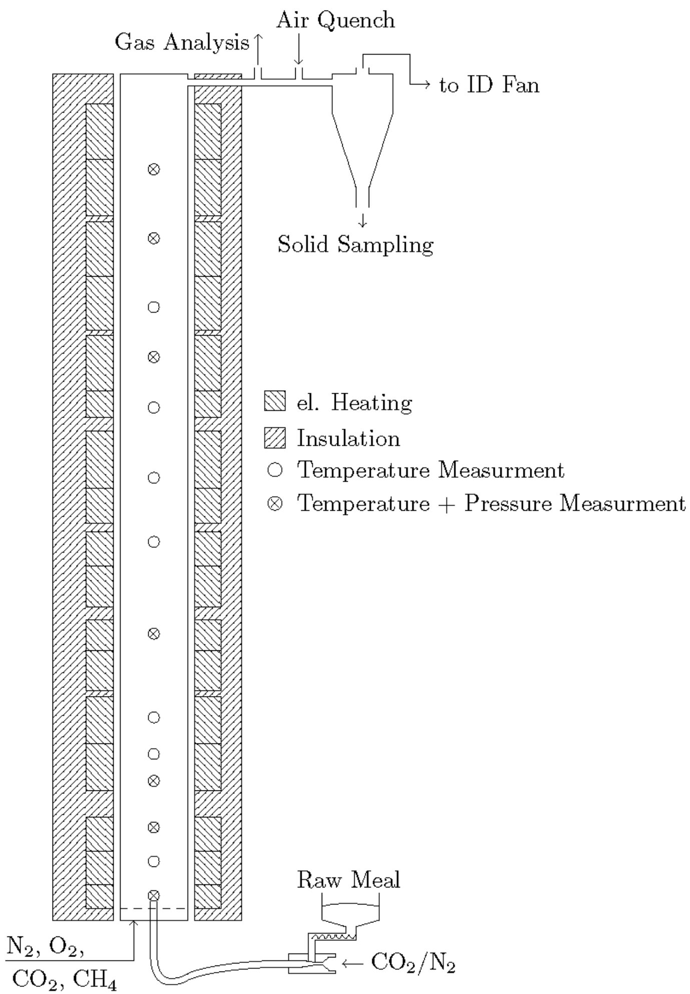
Experimental setup

Experimental set-up



- Energy supply
  - Resistance heating
  - Natural gas combustion
- Raw meal feeding
  - Weight based controlled screw feeder
  - Dispersion by venturi nozzle
- Quench of solids (T_{Gas} <500 °C) to avoid further carbonation /calcination

Experimental set-up



Calcination (EF):

	T_{Calc}	τ_{Solid}	y_{CO2}
Air	860 °C	2 … 6 s	~ 26 vol.%
Oxy-fuel	900 °C 920 °C	2 … 6 s	~ 90 vol.%

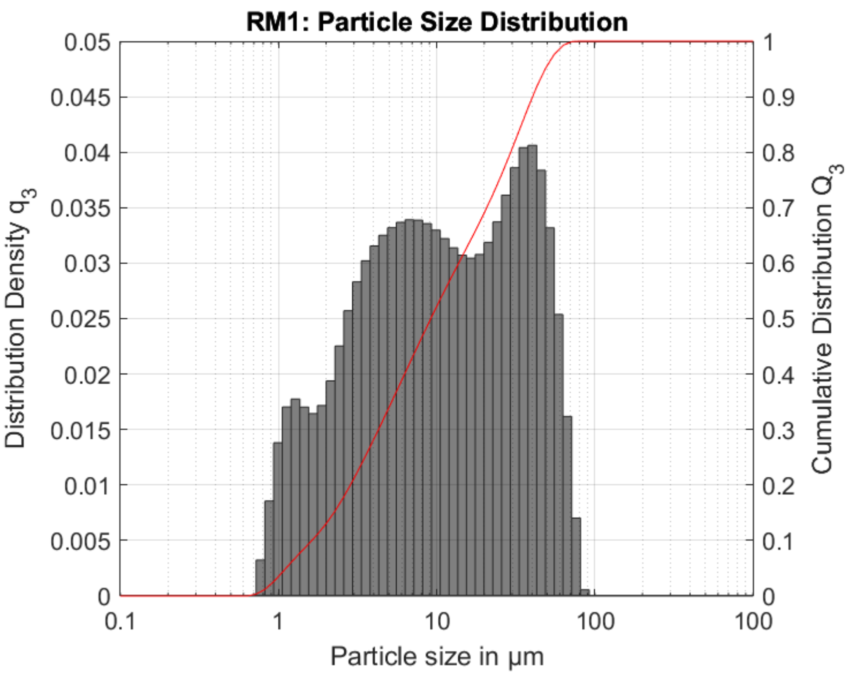
Carbonation (TGA):

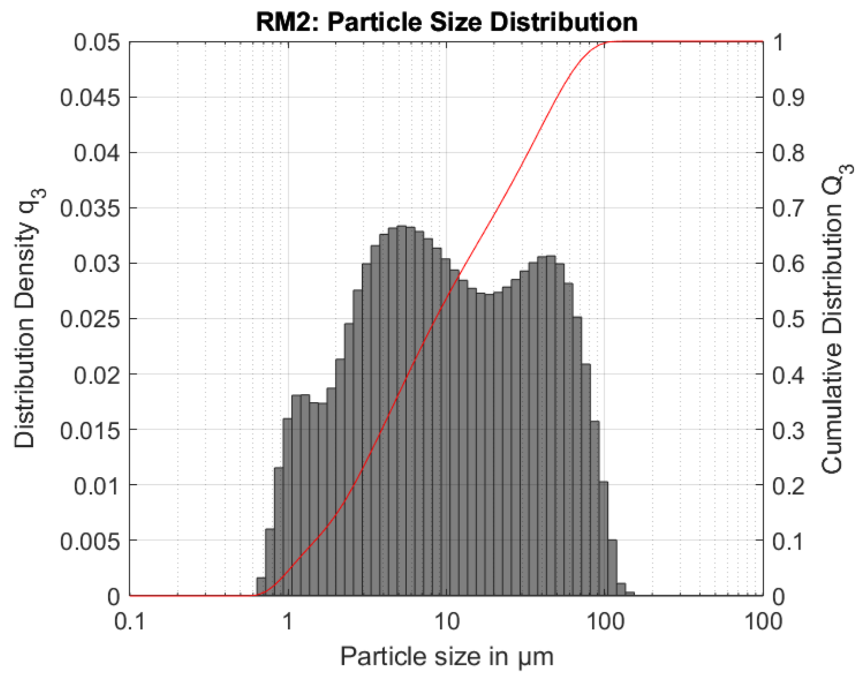
T_{Carb}	y_{CO2}		
600 °C	5 vol.%	10 vol.%	20 vol.%
650 °C			
700 °C			

Experimental set-up

Chemical composition of investigated raw meals

	CaO ($CaCO_3$)	SiO_2	Al_2O_3	Fe_2O_3	LOI
	wt-%, wf				
RM1	41.28 (73.71)	16.73	3.56	2.33	33.08
RM1: Limestone	50.34 (89.90)	2.98	0.91	0.47	43.15
RM1: Marl	37.31 (66.63)	22.45	4.36	1.65	30.24
RM2	40.07 (71.56)	14.39	6.28	1.95	33.49

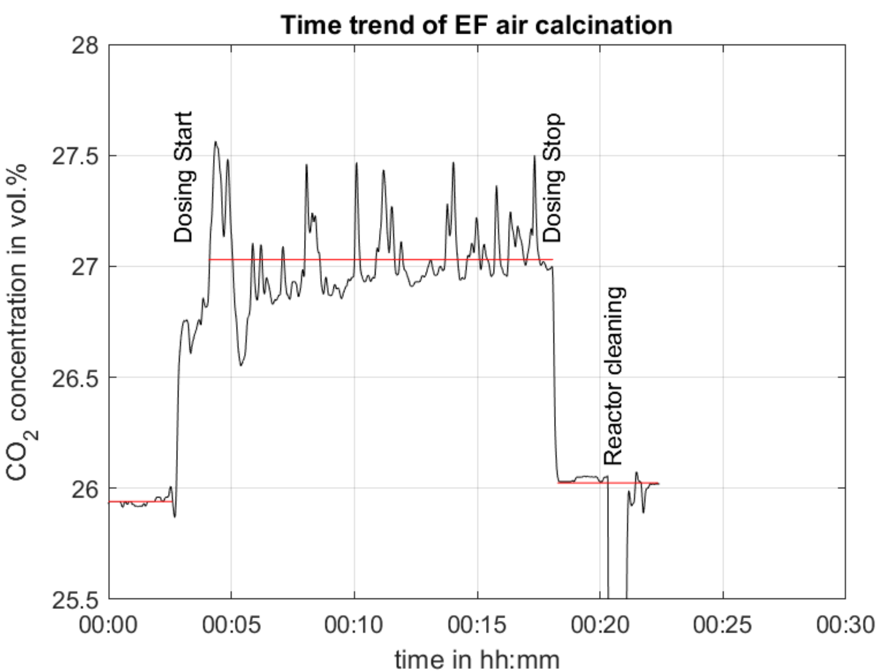


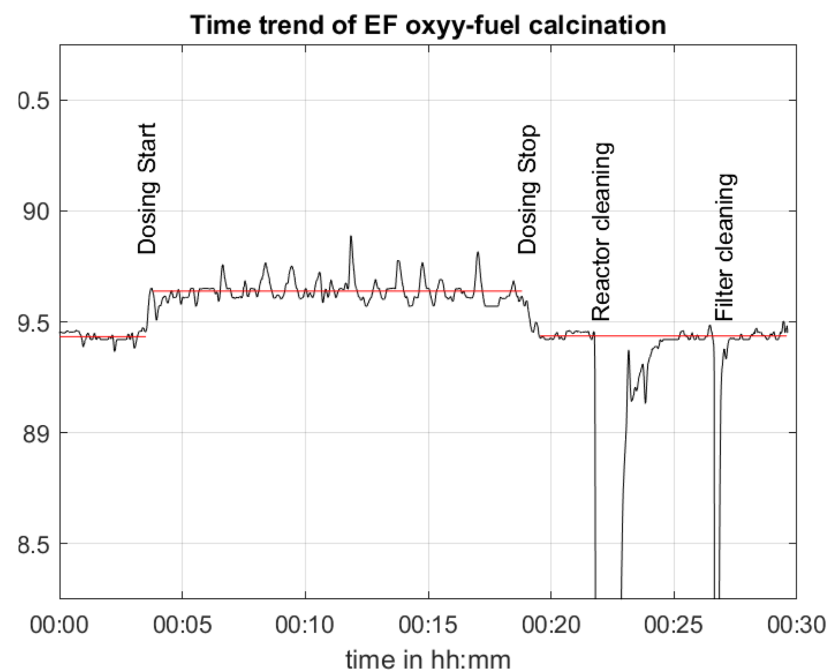


Methodology

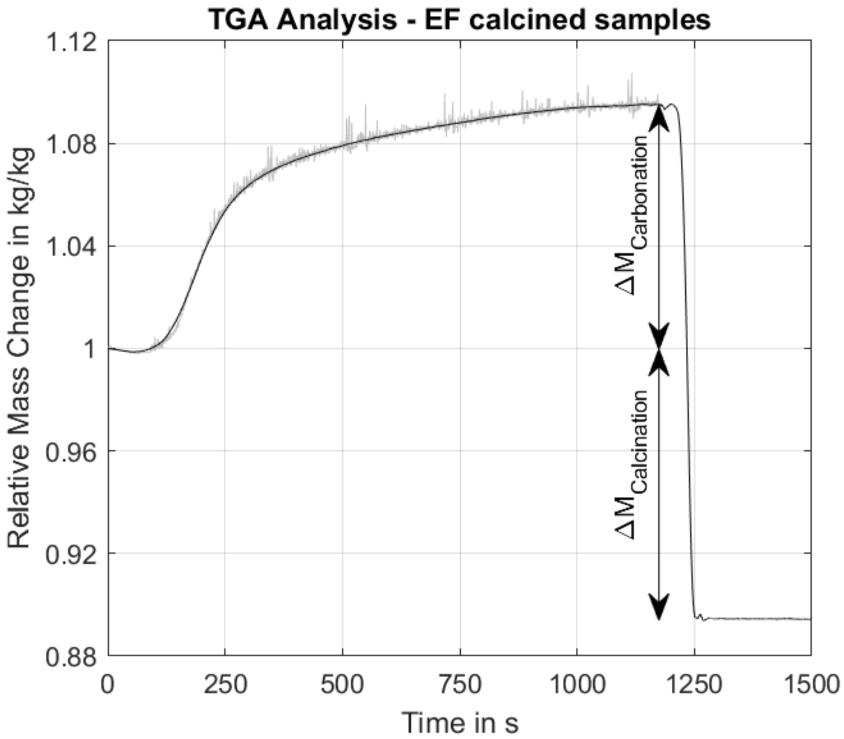
Experimental execution – EF experiments

I. Adjustment of gas concentration for different residence times / velocities
II. Start of raw meal dosing
III. Collection of solid samples after/at cyclone (top of reactor)
IV. Stop of raw meal dosing
V. Reactor and gas filter cleaning





Experimental execution – TGA analysis



- Calcination Degree:

$$x_{Calc} = 1 - \frac{x_{CO_2,Sample} \cdot (1 - x_{CO_2,RawMeal})}{(1 - x_{CO_2,Sample}) \cdot x_{CO_2,RawMeal}}$$

- (Re)Carbonation Degree:

$$\tilde{x} = \frac{N_{CO_2,ReCarb}}{N_{CaO,Sample} - N_{CaCO_3,Sample}}$$

Results

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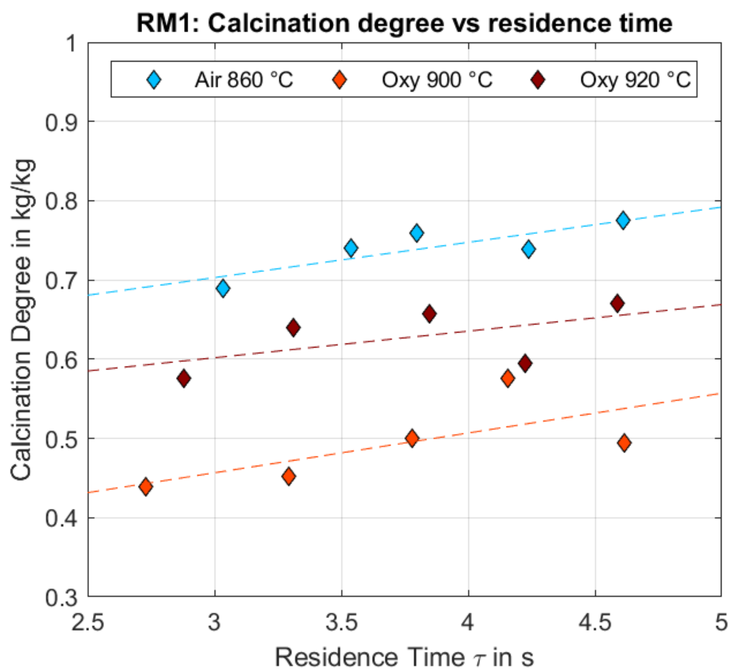
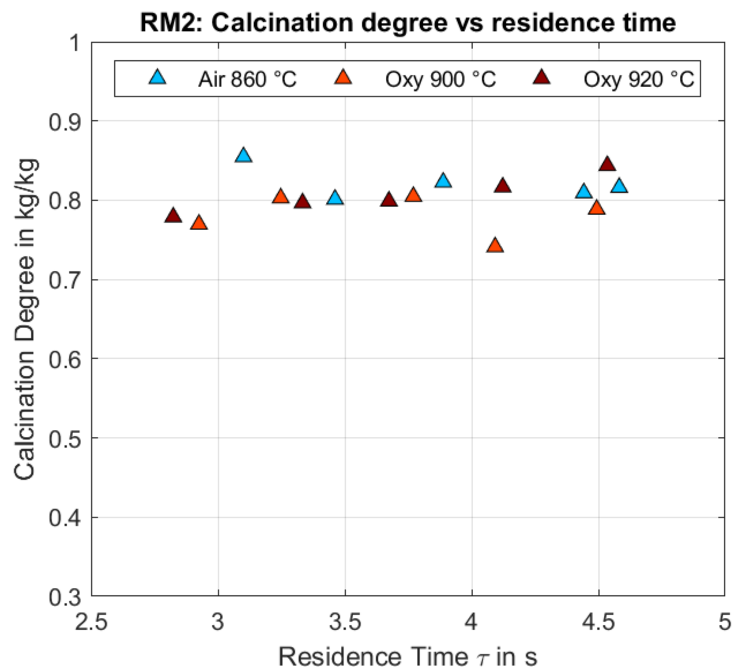
Experimental Results – Calcination

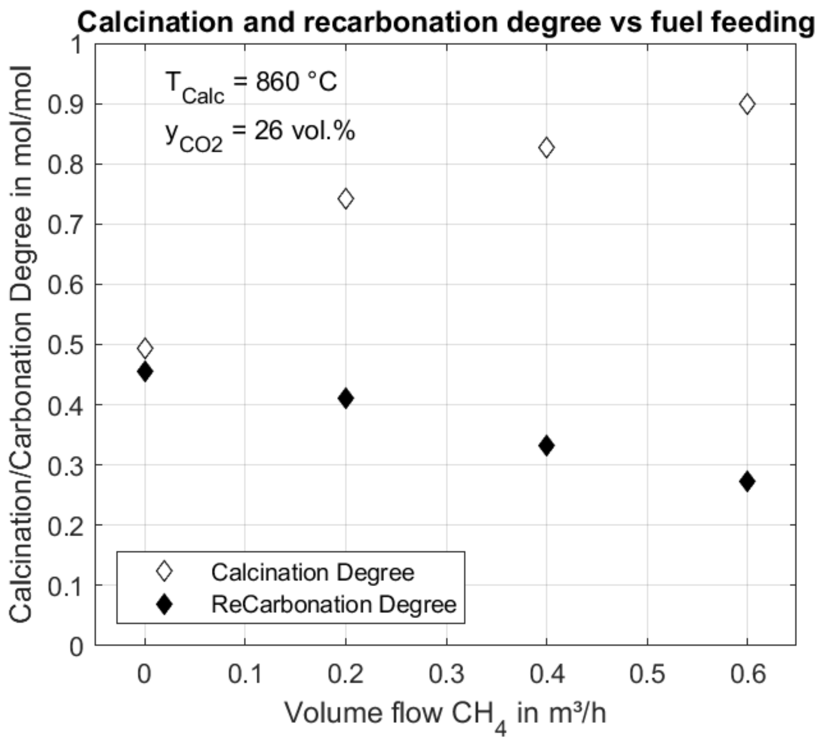




- **Slight increase in calcination degree with residence time**
- **Reduced calcination degree for oxy-fuel calcination**
- **Calcination degree increases with temperature for oxy-fuel for oxy-fuel calcination**

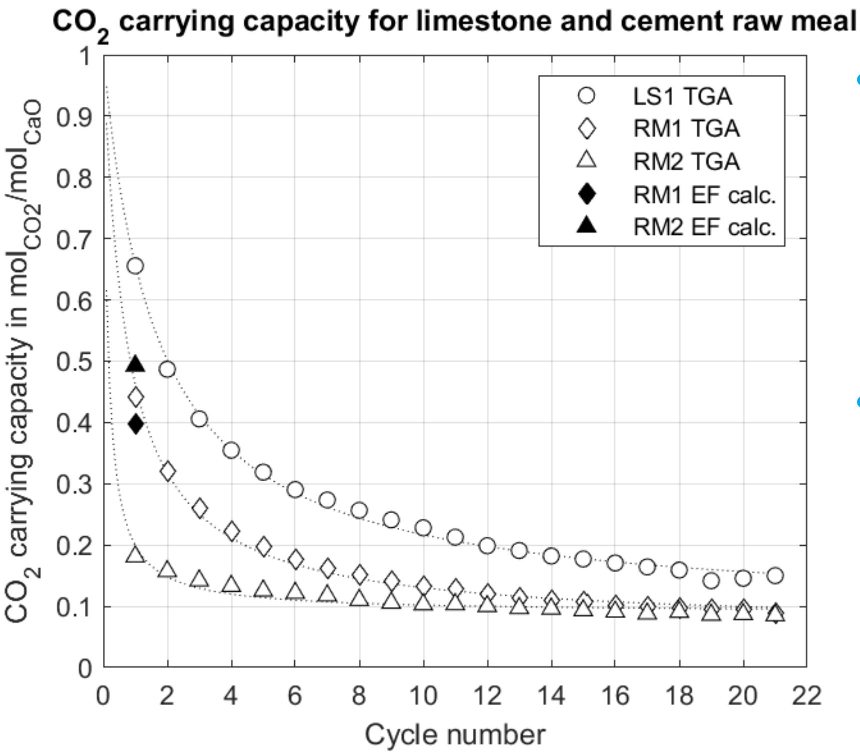
- **High burnability raw meal: Constant calcination degree throughout all experiments**

Experimental Results – Fuel Feeding



- High amount fuel lead to hot spots at reactor bottom
- Improved calcination when fuel is fed into the reactor
  ⇨ Heat transfer by radiation insufficient
- Increased fuel feeding leads to:
  - Increase calcination degree
  - Decreasing recarbonation degree

Experimental Results – CO_2 capture perfomacne

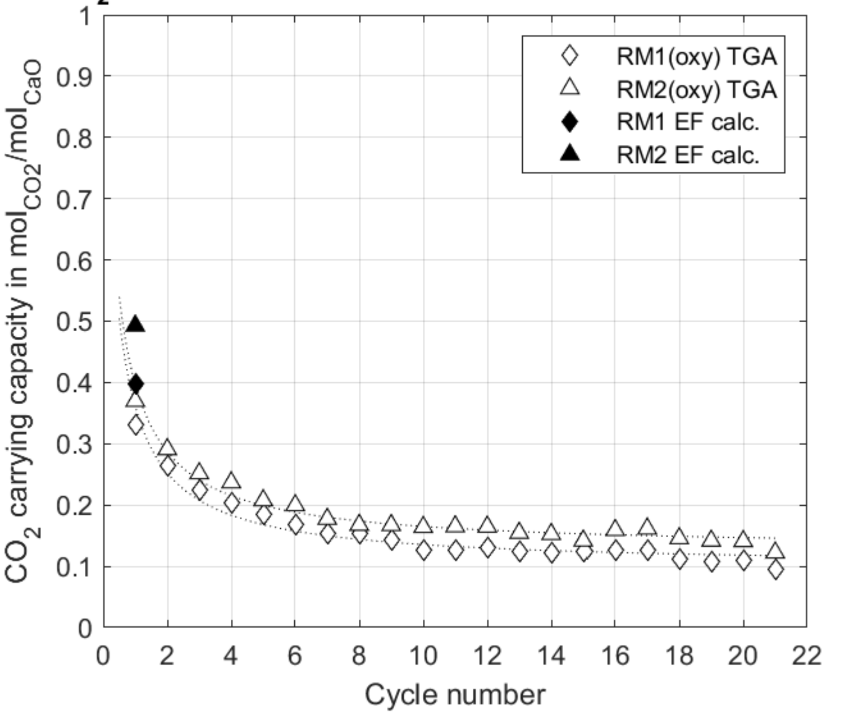


TGA Cycles:
T_{Calc} = 860 °C | τ_{calc} = 10 min | y_{CO2} = 0
T_{Carb} = 650 °C| τ_{Carb} = 10 min | y_{CO2} = 10 vol.%

- **TGA sorbent analysis show reduced CO_2 carrying capacities for cement raw meals**
  - **Belit formation binds CaO**
  - **Marl type raw meal show increased deactivation**
- **Entrained flow calcined samples show**
  - **RM1: slightly lower X_{CO_2}**
  - **RM2: significantly increased X_{CO_2}**

Experimental Results – CO_2 capture perfomacne

CO2 carrying capacity for limestone and cement raw meal



TGA Cycles:

T_{Calc} = 920 °C | τ_{calc} = 10 min | y_{CO2} = 90 vol.%

T_{Carb} = 650 °C| τ_{Carb} = 10 min | y_{CO2} = 10 vol.%

- **RM1: Decrease of CO_2 carrying capacity when oxy-fuel calcined**
- **RM2: Increase of CO_2 carrying capacity for initial cycles**

Sorbent deactivation depended on T_{Calc}, τ_{Calc} and p_{CO_2}

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Conclusions and Outlook

- Belite formation occurs at calcium looping conditions in the oxy-fuel calciner and will consequently deactivated the sorbent
- Belite formation more pronounced for marl type raw meals
- Hot spots during calcination lead to stronger deactivation
- EF calcined sorbent hold sufficient activity to run an EF calcium looping system

- Investigation of further raw meal qualities to achieve a broader data basis and more comprehensive understanding

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Experimental Results – CO_2 uptake