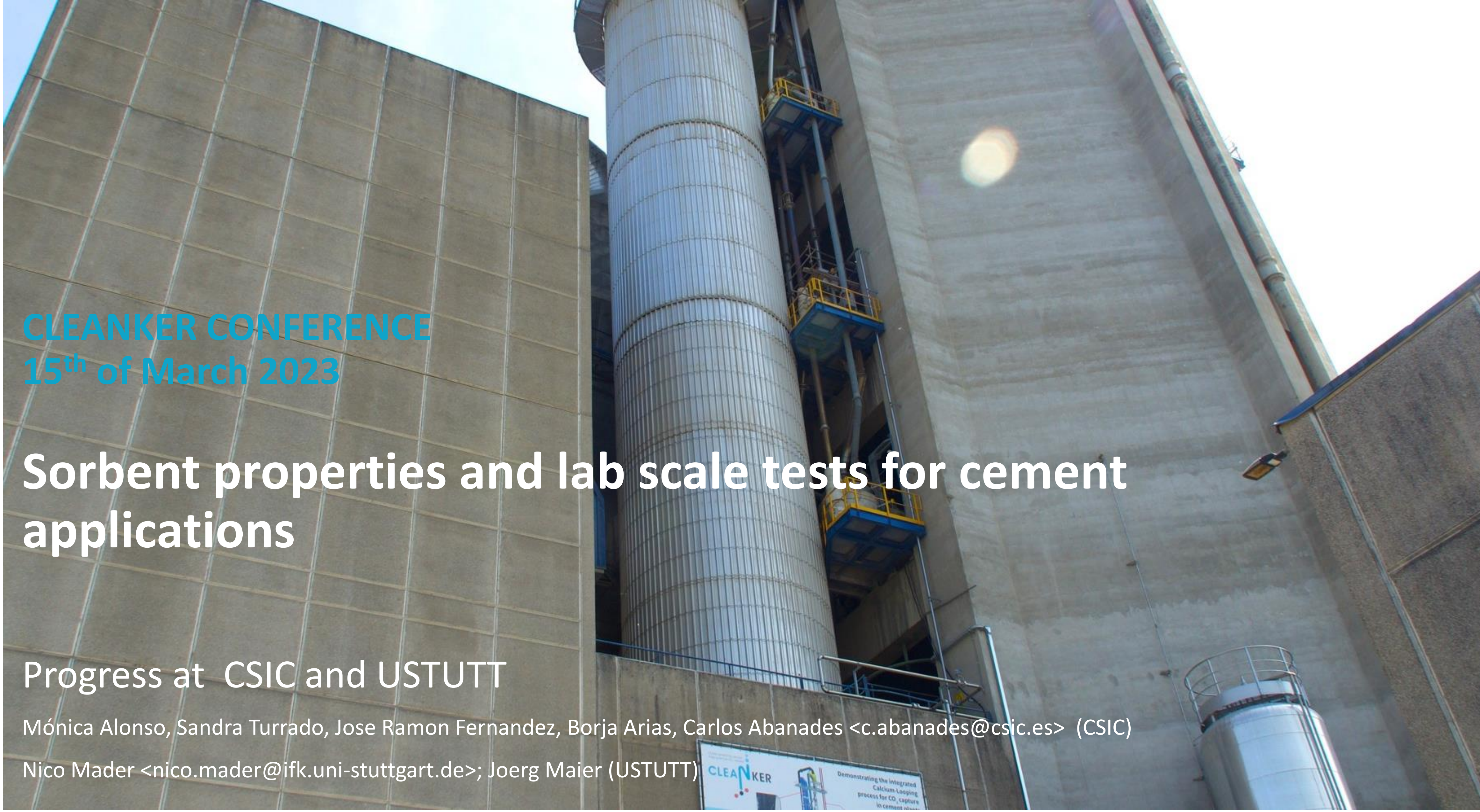

CLEANKER CONFERENCE
15th of March 2023

Sorbent properties and lab scale tests for cement applications

Progress at CSIC and USTUTT

Mónica Alonso, Sandra Turrado, Jose Ramon Fernandez, Borja Arias, Carlos Abanades <c.abanades@csic.es> (CSIC)

Nico Mader <nico.mader@ifk.uni-stuttgart.de>; Joerg Maier (USTUTT)

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- ❑ Calcination kinetics in CO_2-rich atmosphere
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3. Conclusions

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Calcination kinetics of cement raw meals under various CO_2 concentrations

Jose Ramon Fernandez, * Sandra Turrado and Juan Carlos Abanades

I&EC research
Industrial & Engineering Chemistry Research

Article

Cite This: Ind. Eng. Chem. Res. 2019, 58, 5445–5454
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Kinetic Study of Belite Formation in Cement Raw Meals Used in the Calcium Looping CO_2 Capture Process

Mónica Alonso, José Ramón Fernández,* and Juan Carlos Abanades
Spanish Research Council, INCAR-CSIC, Francisco Pintado Fe, n. 26, 33011 Oviedo, Spain

ABSTRACT: Calcium looping technology could be one of the most efficient ways to drastically reduce the carbon footprint of cement manufacture since $CaCO_3$ is a major component of the raw meal used to produce clinker. However

Deactivation by belite formation
Quantification (kinetic model)

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Article

Experimental Investigation of Sulfation Phenomena in Calcium Looping Systems Integrated in Cement Plants

Edoardo De Lena,* Mónica Alonso, and J. Carlos Abanades

Cite This: Ind. Eng. Chem. Res. 2022, 61, 4561–4566

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ABSTRACT: The sulfation phenomena of raw meal materials involved in calcium looping (CaL) applications to capture CO_2

Carbonation of Fine CaO Particles in a Drop Tube Reactor

Sandra Turrado, Borja Arias, José Ramón Fernández,* and Juan Carlos Abanades
Spanish Research Council, INCAR-CSIC, Francisco Pintado Fe, n. 26, 33011 Oviedo, Spain

ABSTRACT: The calcium looping technology using entrained flow reactors seems particularly suited for integration in cement plants due to the fine particle diameters and high gas velocities that are characteristic of these plants. However, there is little experimental information available in the literature on the carbonation performance

ACS OMEGA

Cite This: ACS Omega 2018, 3, 15229–15234
http://pubs.acs.org

Characterization of a Marl-Type Cement Raw Meal as CO_2 Sorbent for Calcium Looping

Mónica Alonso,*[†] Mathias Hornberger,[‡] Reinhold Spörl,[‡] Günter Scheffknecht,[‡] and Carlos Abanades[†]
[†]Spanish Research Council, CSIC-INCAR, C/ Francisco Pintado Fe, 26, 33011 Oviedo, Spain
[‡]IFK—Institute of Combustion and Power Plant Technology, University of Stuttgart, Pfaffenwaldring 23, 70569 Stuttgart, Germany

ABSTRACT: The use of cement raw meals as sorbent precursors for CO_2 capture can

Main experimental facilities used at CSIC for CaL gas-solid reactions involving raw meals

- CO_2 carrying capacity
- Belite formation kinetics
- Calcination kinetics
- Carbonation kinetics
- Sulfation kinetics

Thermogravimetric analysers

TA-Q5000IR

In-house TGA

Reactions with time scales >10 s

Solids/ Carrier gas

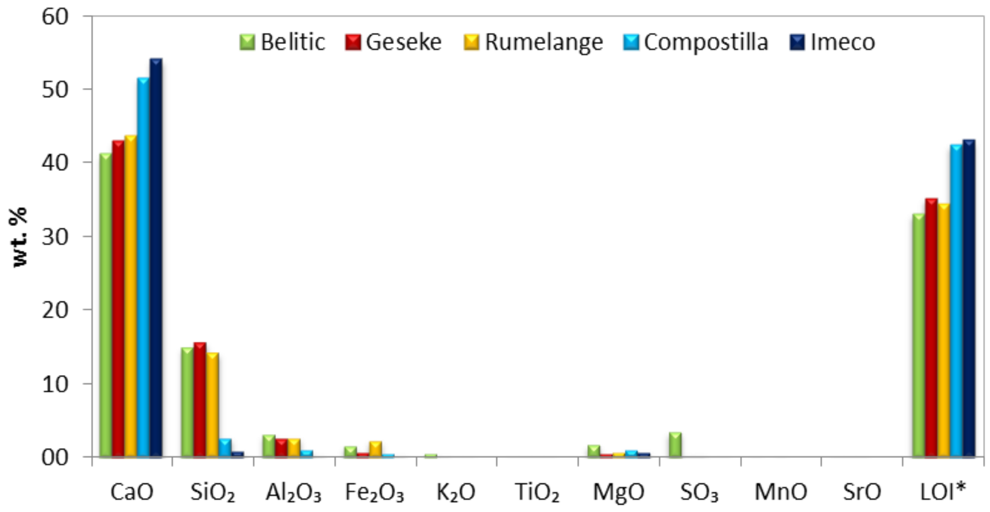
$T/CO_2/O_2$
Solids sampling

scales <10 s

13 Calcium-based raw meals materials

- **Rumelange**: mixture of marl, limestone and slag
- **Belitic**: mixture of marl, limestone and gypsum
- **Geseke**: mixture of marl and a corrective material (4 wt.%)
- **Compostilla**: limestone (<20 µm, 20-36 µm, 36-63 µm)
- **Imeco**: limestone (<20 µm, 20-36 µm, 36-63 µm)
- **Vernasca**: mixture of marl (Marine) and limestone (Calcare)
- **Marine**: marl
- **Calcare**: limestone
- **Bilbao**: marl

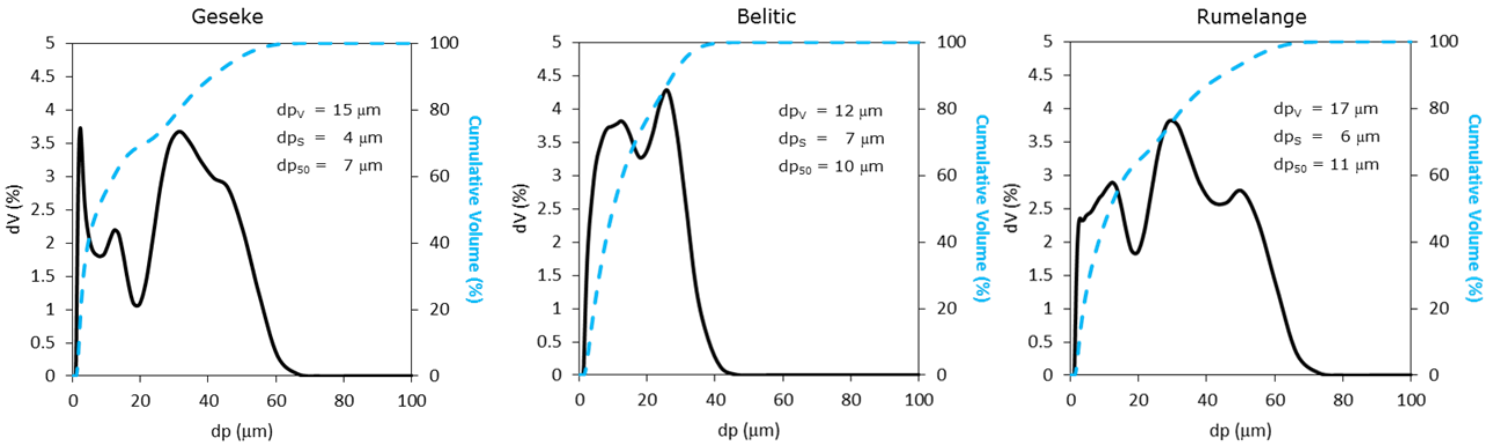
Chemical composition (XRF)



- Similar contents of CaO (41-43 wt.%), SiO_2 (15 wt.%) and Al_2O_3 (3 wt.%) in the raw meals
- Relevant content of Fe_2O_3 (2.3 wt.%) in Rumelange (presence of slag)
- High content of SO_3 (3.5 wt.%) in Belitic (presence of gypsum)

Physical and chemical characterisation of raw meals

Particle size distribution



- Clearly separated volumetric fractions
- Similar average diameters (not expected diff. behaviour due to particle size)

BET surface area

Material	BET area (m^2/g)
Raw meals/marls	
Vernasca	13.5
Rumelange	6.1
Belitic	10.8
Bilbao	3.6
Geseke	4.3
Marine	13.7
Limestones	
Calcare	1.4
Compostilla <20 µm	4.0
Compostilla 20-36 µm	4.0
Compostilla 36-63 µm	3.1
Imeco <20 µm	0.6
Imeco 20-36 µm	0.6
Imeco 36-63 µm	0.4

- Limestones present in general the lowest BET areas (0.4-4 m^2/g). BET areas increase as d_p is reduced (for d_p>20 µm)
- Intermediate values (3.6-6.1 m^2/g) for Bilbao (marl), Geseke (marl) and Rumelange (mixture)
- Largest BET areas (11-13.7 m^2/g) for Belitic (mixture), Marine (marl) and Vernasca (mixture).

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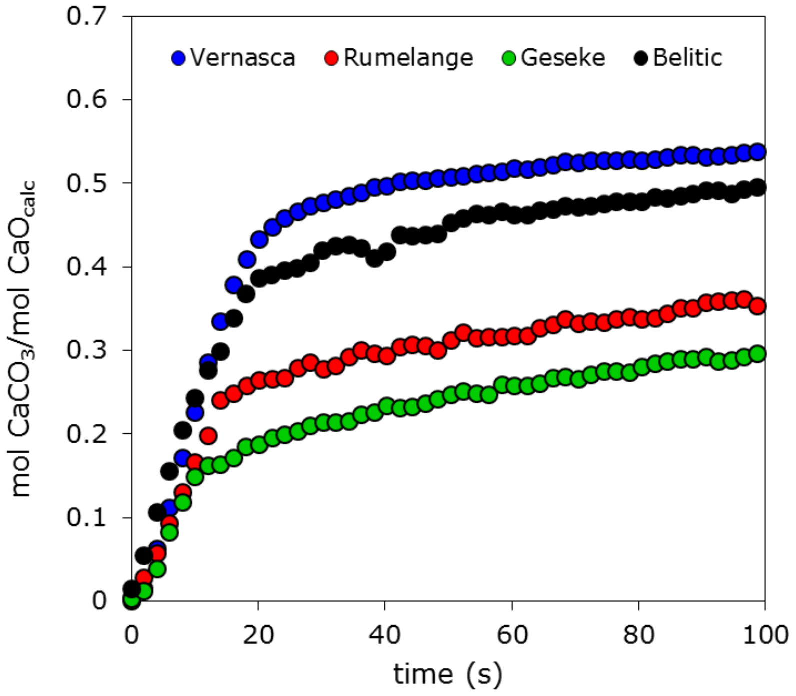
CO_2 carrying capacity tests with differente raw meals



- Materials with higher **Ca-Si aggregation level** show lower **CO_2 carrying capacities** (formation of belite)
- **Geseke** (almost single compound raw meal) shows the lowest CO_2 carrying capacity
- **Belitic** (mixture) exhibits similar behaviour to Vernasca (i.e. similar Ca-Si aggregation level)
- **Rumelange** (mixture) presents lower carbonation conversion than expected. Possible formation of other compound/s that consume active CaO (due to unknown crystalline phase detected by XRD?)

Co-funded by the Horizon 2020 Framework Programme of the European Union

Reactivity of calcined Vernasca raw meal towards CO_2 (from TG experiments)

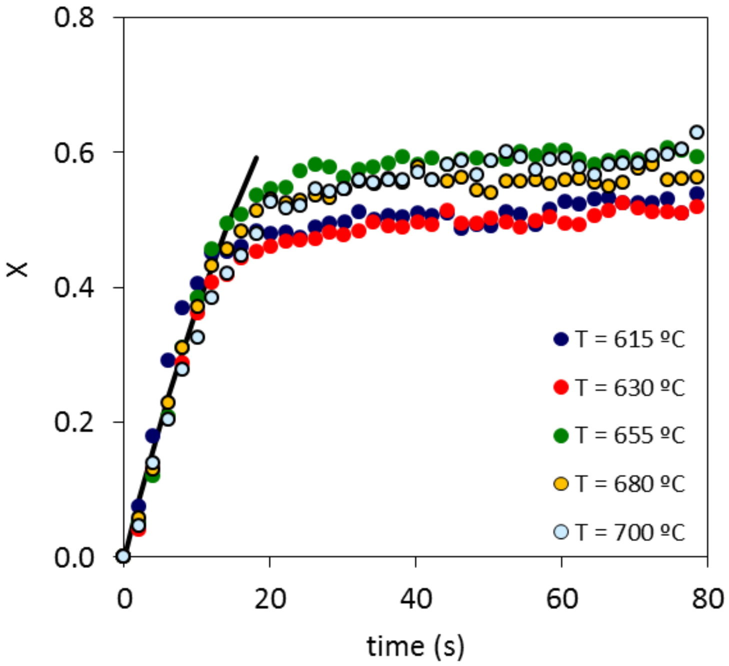
- Carbonation expe. and tuning of kinetic model for Vernasca

In the reported range values

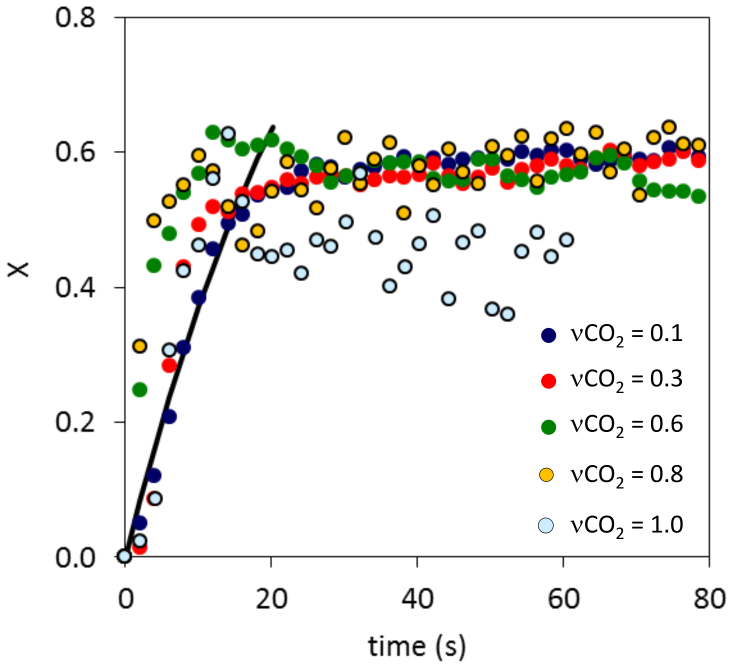
$$X_{carb} = 1 - \left(1 - k_{carb}\left(\nu_{CO2} - \nu_{eq}\right)t\right)^3$$

$k_{0,carb}$ = 4.61 s^{-1}; Ea = 26 kJ/mol

10 vol% CO_2 in air



T_{carb} = 655 ºC



- Similar tendencies than those observed for CaO derived from limestone in the fast stage.
- The CO_2 concentration greatly affects the carbonation rate.

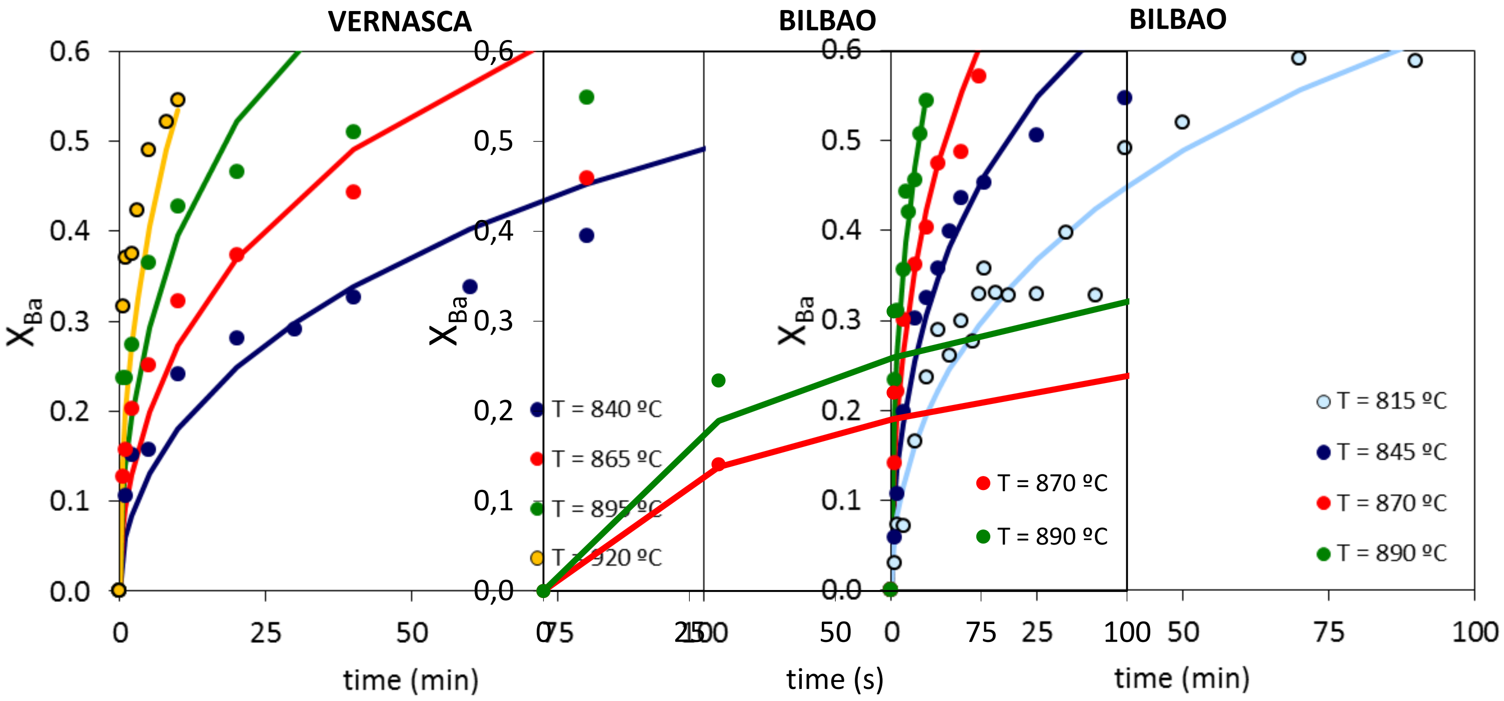
Co-funded by the Horizon 2020 Framework Programme of the European Union

Kinetics of Belite formation (from TG experiments)

- Extent of belite formation during the calcination of Vernasca

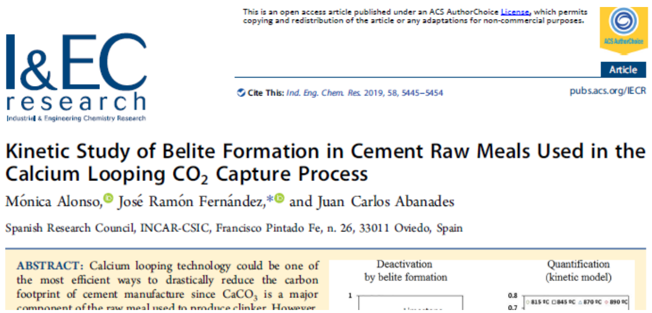
$$2\,CaO + SiO_2 \longrightarrow Ca_2SiO_4$$

$$X_B = 1 - \left[1 - (k_B t)^{1/2}\right]^3$$



	k_0 (s^{-1})	E_a (kJ/mol)
Before calcination	6.64	133
After calcination	4.35×10^{10}	336

Similar value to Weisweiler et al.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Kinetic Study of Belite Formation in Cement Raw Meals Used in the Calcium Looping CO2 Capture Process

Mónica Alonso, José Ramón Fernández,* and Juan Carlos Abanades

Spanish Research Council, INCAR-CSIC, Francisco Pintado Fe, n. 26, 33011 Oviedo, Spain

ABSTRACT: Calcium looping technology could be one of the most efficient ways to drastically reduce the carbon footprint of cement manufacture since CaCO3 is a major component of the raw meal used to produce clinker. However

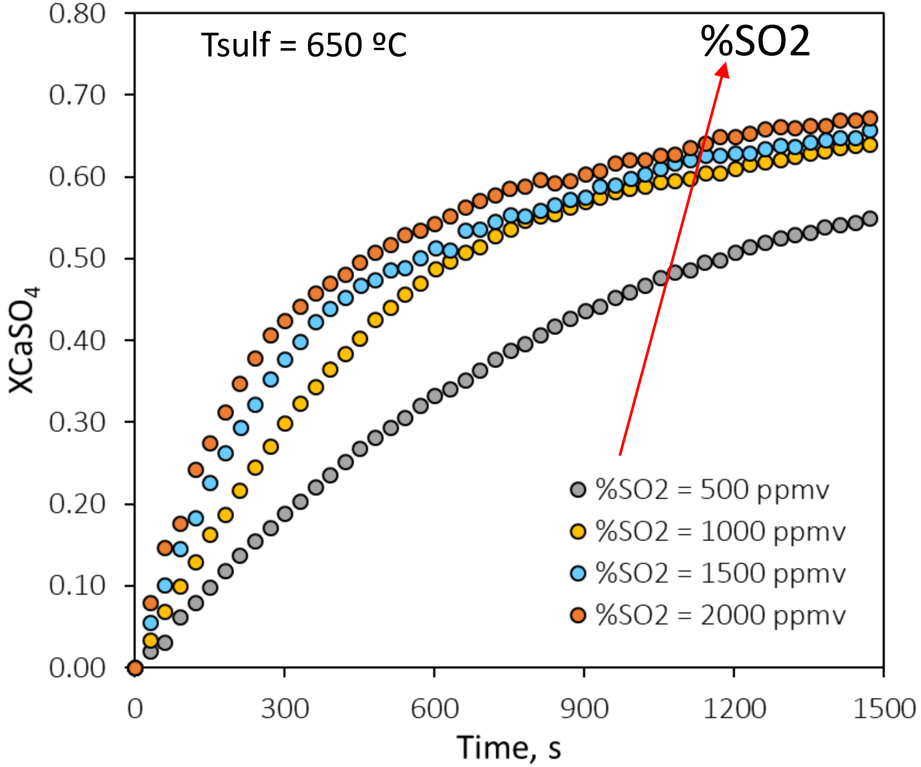
Deactivation by belite formation

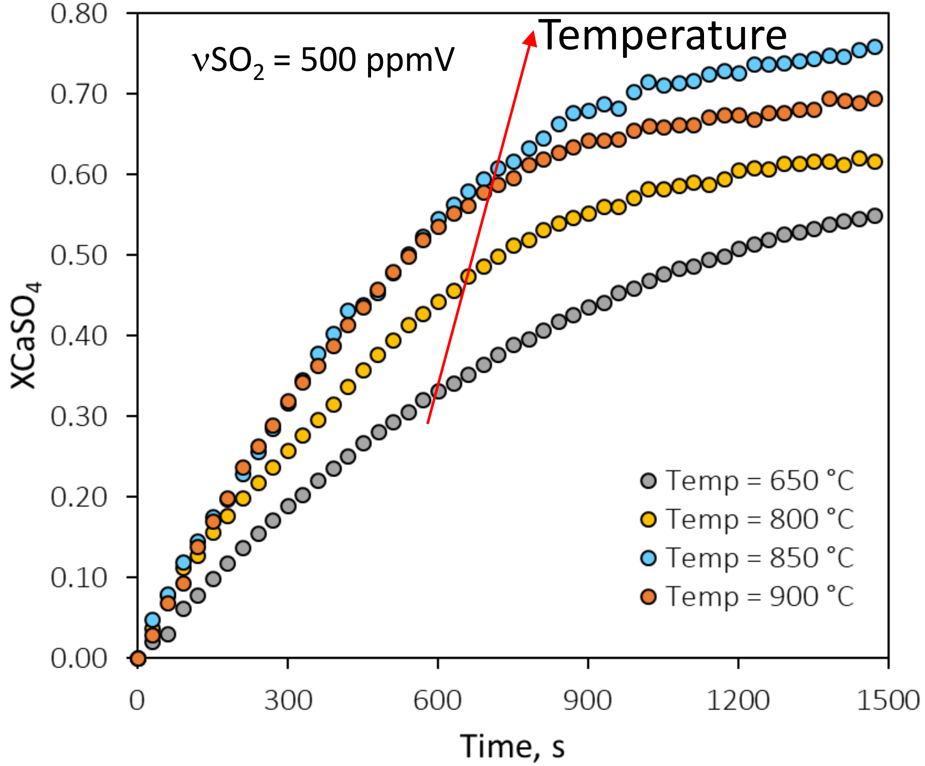
Quantification (kinetic model)

- Calcination temperature greatly affects the reaction.
- In Vernasca raw meal (low level of Ca/Si aggregation) the model overestimates belite formation at long times
- Belite formation in Bilbao raw meal (marl) is accurately described

Kinetics of $CaSO_4$ formation (from TG experiments)

- **Effect of sulfation temperature and SO_2 concentration on Vernasca (non belite)**



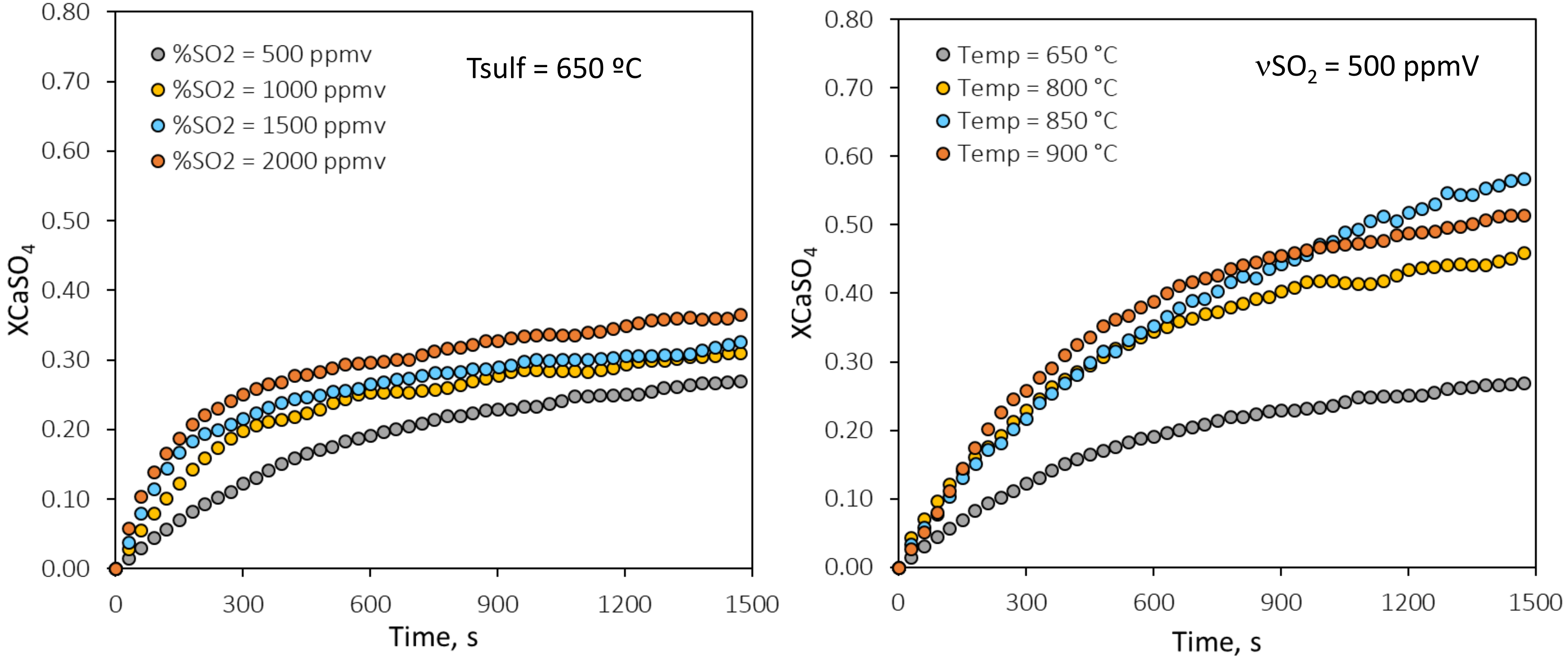


There is an increase in sulfation as the sulphur content in the flue gas increases

There is also an increase in sulfation as the temperature increases. But the maximum was achieved at 850 ºC

Kinetics of $CaSO_4$ formation (from TG experiments)

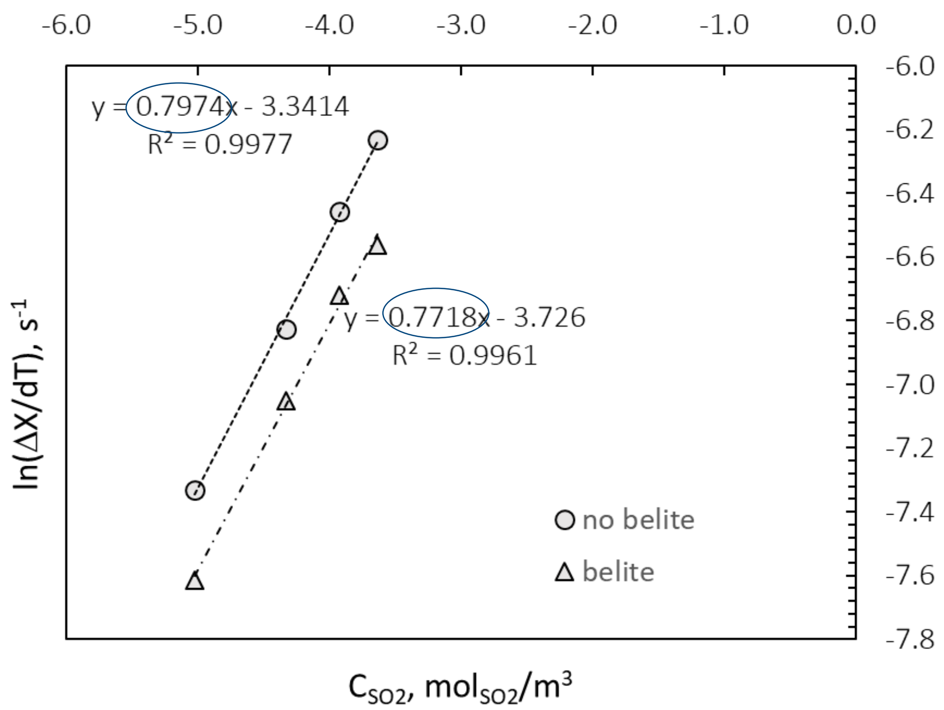
- **Effect of sulfation temperature and SO_2 concentration on Vernasca (<u>maximum belite</u>)**



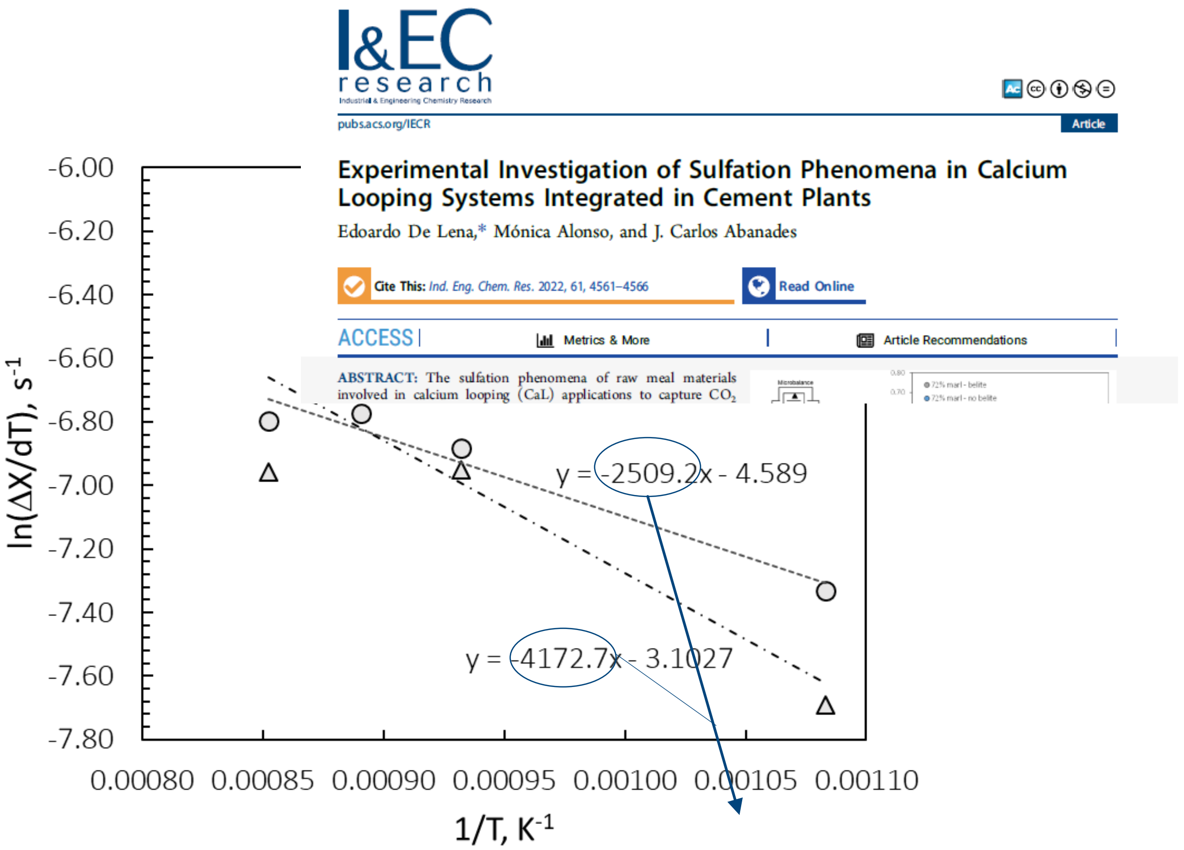
The shape of the obtained curves are the same but with a <u>lower conversion</u>, due to the presence of the <u>belite</u>

Sulfation study: reported in D5.2

- **Kinetic regime parameters**



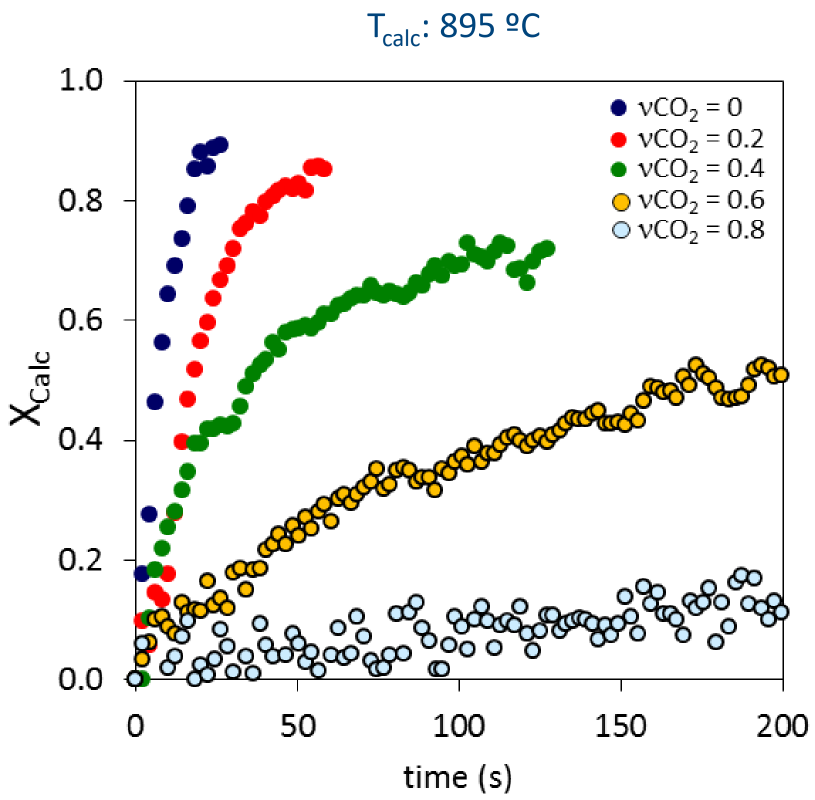
Apparent reaction order of 0.8
(very similar to a reaction order for a limestone between 0.6 – 1)



Activation energy for the kinetic regime between 20.9 kJ/mol and 34.7 kJ/mol
(very similar to Eact for a limestone between 20-41 kJ/mol)

Kinetics of Calcination (from TG experiments)

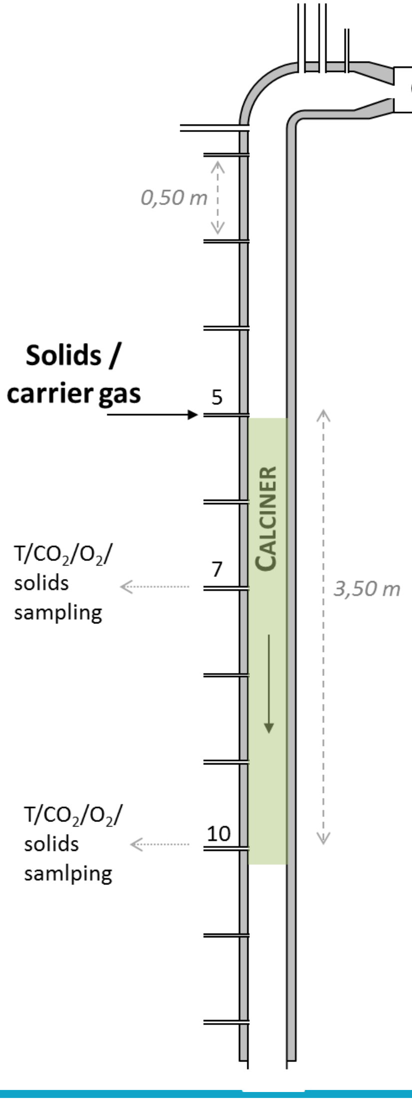
- Calcination experiments with Vernasca



- Much longer calcination times than those found in suspension reactors.
- Heat transfer resistance has been identified as the main limitation to measure reliable kinetics of very fast reactions.

Kinetic studies of (fast) calcination of raw meals in a drop tube

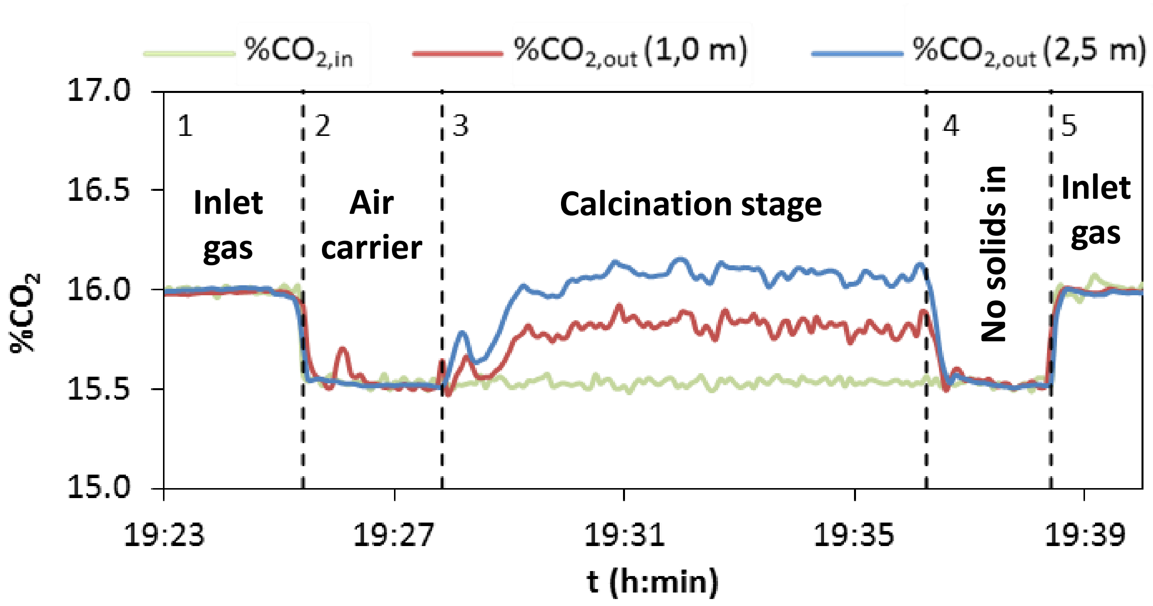
Experimental methodology



Main operating conditions tested in the drop tube

Calciner temperature (°C)	T_{calc}	790-1000
Calciner inlet velocity (m/s)	u_{calc}	1.1 - 2.2
Inlet CO_2 to the calciner	vol.%	0 - 90
Solids flowrate (kg/h)	$\dot{m}_s$	0.2 - 1.0

Pulverized coal was mixed (up to 10% wt) with raw meals for tests at T>900ºC

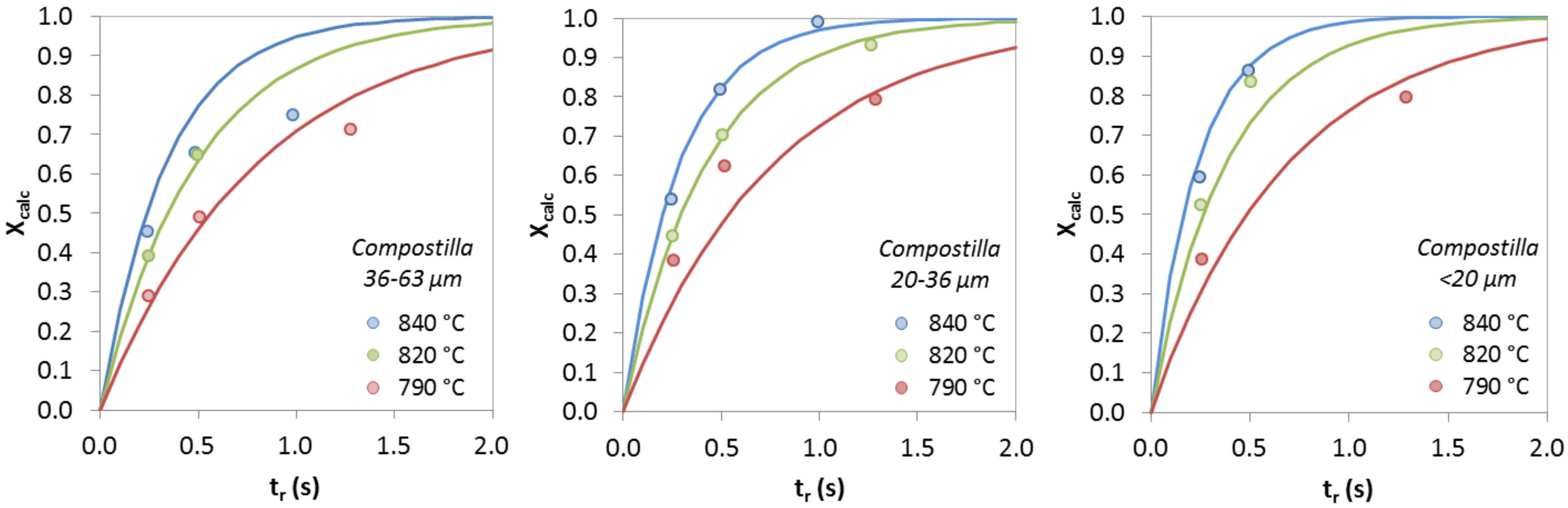


Experimental conditions (reference test): material Compostilla 36-63 µm, T= 860 ºC, $u_{gas=}$2 m/s, solids,in =0.65 kg/h, $\%CO_2$in=15.5

Co-funded by the Horizon 2020 Framework Programme of the European Union

2. Experimental results: kinetic studies of calcination

Effect of **particle size and surface area** on calcination kinetics



- Higher surface BET areas accelerate the calcination of $CaCO_3$
- Calcination in air (0 vol.% CO_2) ,T= 820 ºC and t_r =0.5 s:

Compostilla 36-63 µm (S_{BET}= 3.1 m^2/g) → X_{cal}=0.60
Compostilla 20-36µm (S_{BET}= 4.0 m^2/g) → X_{cal}=0.70
Compostilla <20 µm (S_{BET}= 4.0 m^2/g) → X_{cal}=0.70

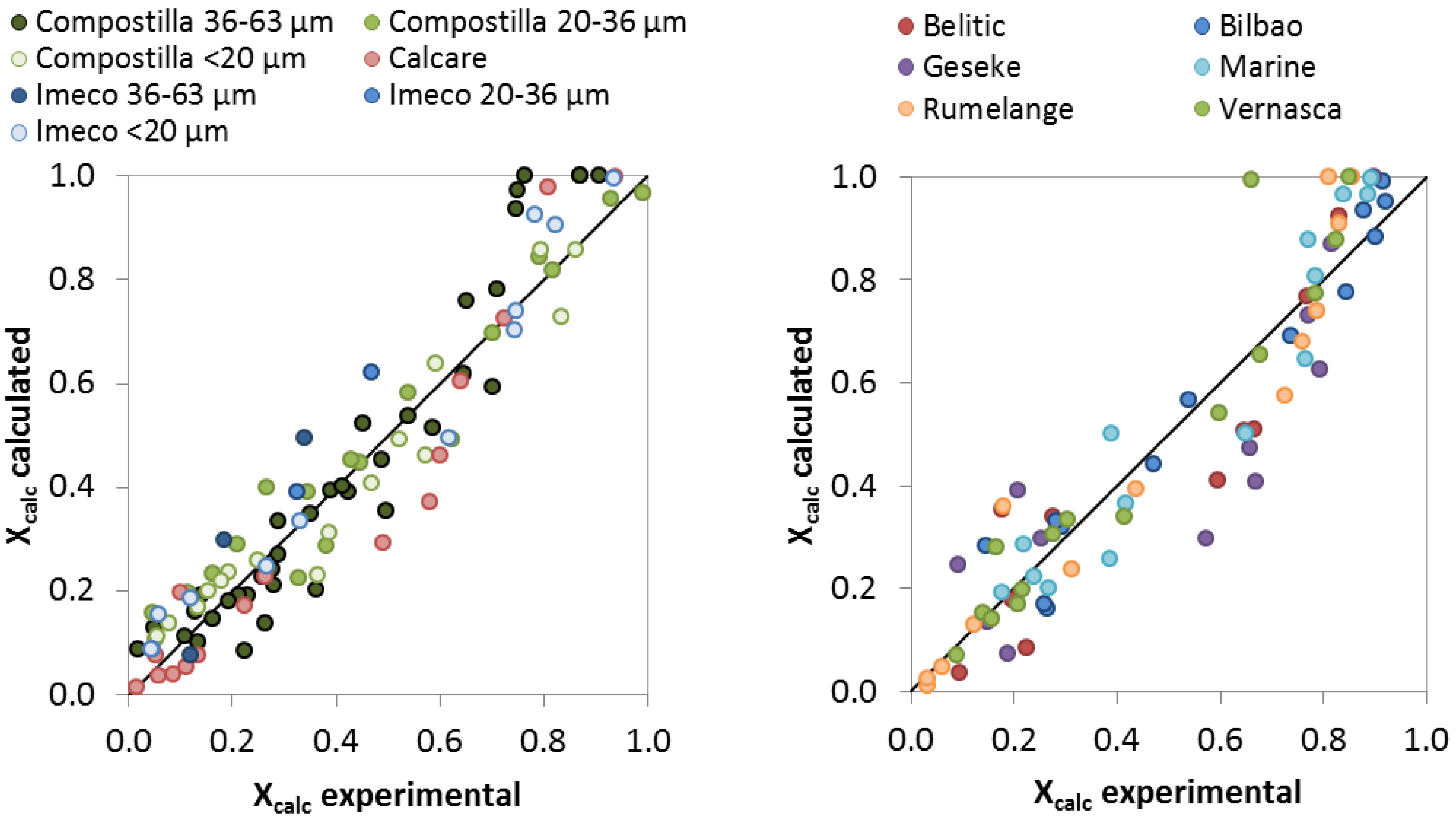
RESULTS CONSISTENT WITH BORGWARD´S MODEL (1985)

(calcination in atmospheres free of CO2)

Co-funded by the Horizon 2020 Framework Programme of the European Union

2. Kinetic studies of calcination

Experimental vs. model



- The model predicts reasonably well the extent of the solids conversion for all the materials tested in this study ($r^2 \approx 0.90$)

2. Kinetic studies of calcination

Kinetic model

Borgwardt (1985): $X_{calc} = 1 - e^{-k_1 S_g t_r}$

Valverde et al. (2015): $\beta(T, P_{CO2}) = k_1 \left(1 - \frac{\nu_{CO2}}{\nu_{CO2,eq}}\right) \frac{1}{1 + K_1 \frac{\nu_{CO2}}{\nu_{CO2,eq}}}$

$$X_{calc} = 1 - e^{-a_1 e^{(-E_1/RT)} \left(1-\frac{\nu_{CO2}}{\nu_{CO2,eq}}\right) \frac{1}{1+A_1 e^{(-\Delta_1 H^0/RT)} \frac{\nu_{CO2}}{\nu_{CO2,eq}}} S_g t_r}$$

194.5 kJ/mol (Borgwardt, 1985)

150 kJ/mol (Valverde et al., 2015)

Material	a_1 (mol/m²s)	A_1 (-)
Compostilla	$11.7\cdot10^6$	$153\cdot10^6$
Imeco	$45.8\cdot10^6$	$152\cdot10^6$
Calcare	$11.9\cdot10^6$	$219\cdot10^6$
Vernasca	$2.9\cdot10^6$	$137\cdot10^6$
Marine	$3.0\cdot10^6$	$43\cdot10^6$
Geseke	$5.8\cdot10^6$	$66\cdot10^6$
Rumelange	$4.9\cdot10^6$	$239\cdot10^6$
Belitic	$1.6\cdot10^6$	$28\cdot10^6$
Bilbao	$9.6\cdot10^6$	$27\cdot10^6$

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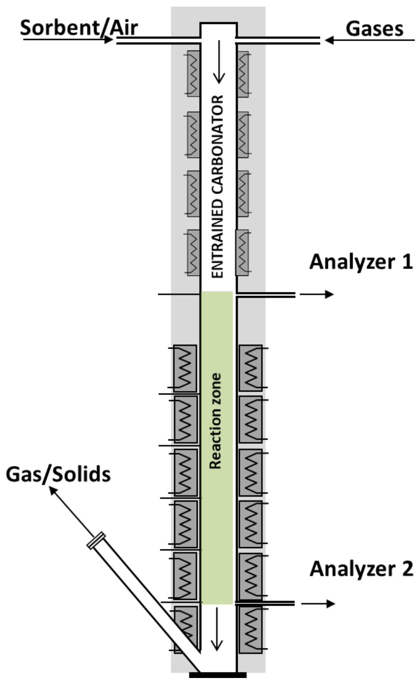
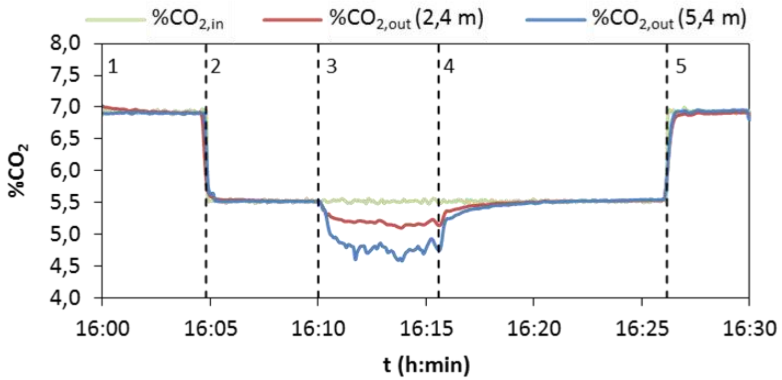
Calcination kinetics of cement raw meals under various CO_2 concentrations

2. Kinetic studies of carbonation

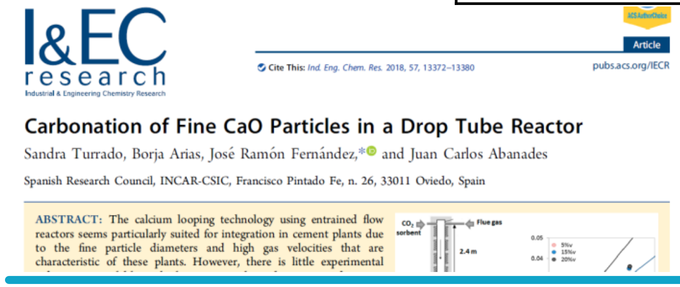
Experimental methodology





Main operating conditions tested in the drop tube

Carbonator temperature (°C)	T_{carb}	590 - 720
Inlet velocity (m/s)	u_{carb}	0,5 - 2,0
Inlet CO_2 to carbonator	v_{CO2}	0,05 - 0,30
Inlet H_2O to carbonator	v_{H2O}	0 - 0,25
X_{ave}	X_{ave}	0,17 - 0,67
Solid flow rate(kg/h)	$\dot{m}_s$	0,3 - 8,0
dp_{50} (µm)	d_{p50}	48 - 53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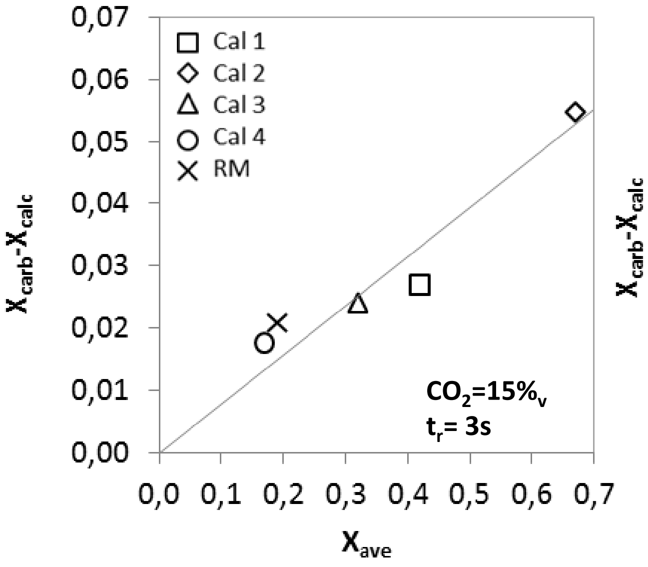
Carbonation of Fine CaO Particles in a Drop Tube Reactor

Sandra Turrado, Borja Arias, José Ramón Fernández,* and Juan Carlos Abanades

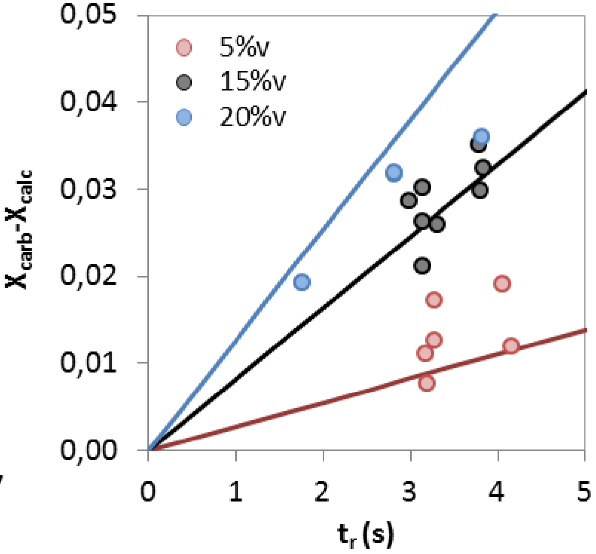
Spanish Research Council, INCAR-CSIC, Francisco Pintado Fe, n. 26, 33011 Oviedo, Spain

ABSTRACT: The calcium looping technology using entrained flow reactors seems particularly suited for integration in cement plants due to the fine particle diameters and high gas velocities that are characteristic of these plants. However, there is little experimental

Effect of X_{ave} on carbonation conversion



Effect of CO_2 concentration on carbonation conversion



Basic carbonation kinetic model

$$\left(\frac{dX}{dt}\right)_{Reactor} = k_s \varphi X_{ave}\left(\overline{\upsilon_{CO2}} - \upsilon_{CO2\,eq}\right)$$

0.16 s^{-1} (in agreement with values reported in the literature)

1. Sorbent studies at USTUTT: Cycle experiments

Properties of cycle experiments:

- TGA conditions set in order to represent entrained flow conditions as good as possible

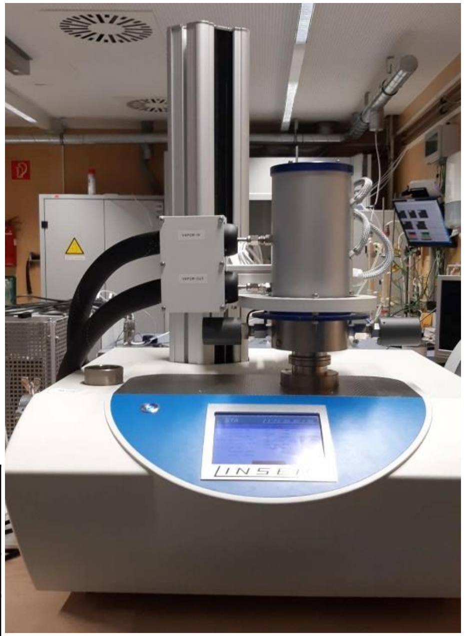
→ Fast heat up and cool down ramps

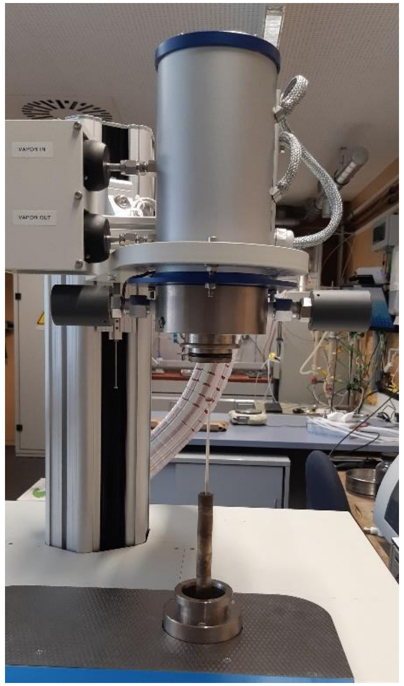
→ Short dwell time at calcining conditions

- Oxy-fuel and air calcination
- Sample weight of approx. 12 mg
- Investigated raw meals:
  - Vernasca raw meal
  - Bilbao
  - Geseke
  - Rumelange
  - Vernasca Calcare

	Vernasca	Bilbao	Geseke	Rumelange	Vernasca Calcare
γ_{CaO}	0,4127	0,4007	0,4345	0,4576	0,5035
γ_{SiO2}	0,1673	0,1439	0,1455	0,1367	0,0298
γ_{Fe2O3}	0,0233	0,0195	0,0089	0,0253	0,0047
γ_{Al2O3}	0,0356	0,0628	0,0227	0,0272	0,0091
γ_{MgO}	0,0121	0,0138	0,0044	0,0018	0,0176
γ_{CO2}	0,3307	0,3349	0,3704	0,3371	0,4315
γ_{others}	0,0184	0,0245	0,0135	0,0142	0,0039

Experimental setup





Linseis STA PT 1100

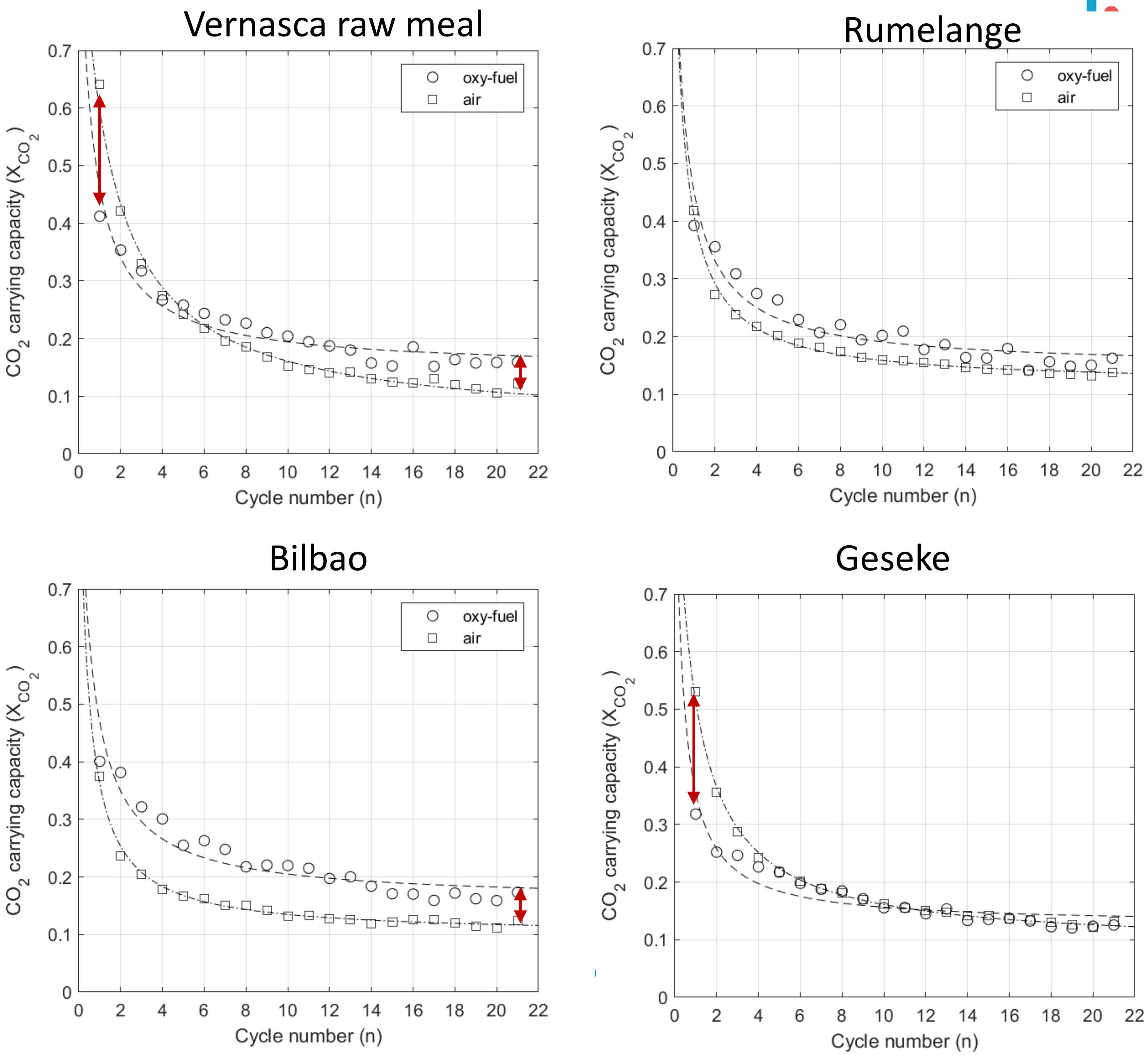
1. Sorbent studies at USTUTT: Cycle experiments

Results:

- Initial deactivation & residual activity

→ appear to be dependent from the reaction atmosphere

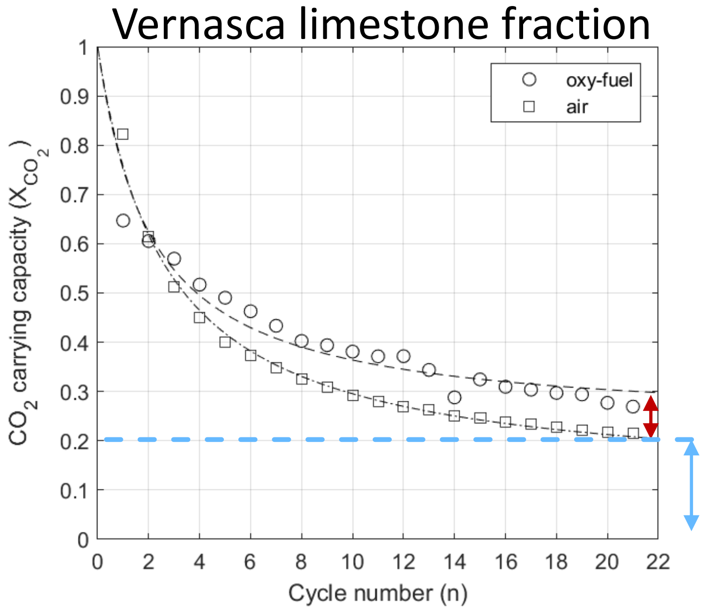
- Cycles with oxy-fuel calcination show higher residual activity
- Different properties between the raw meals have big impact on results

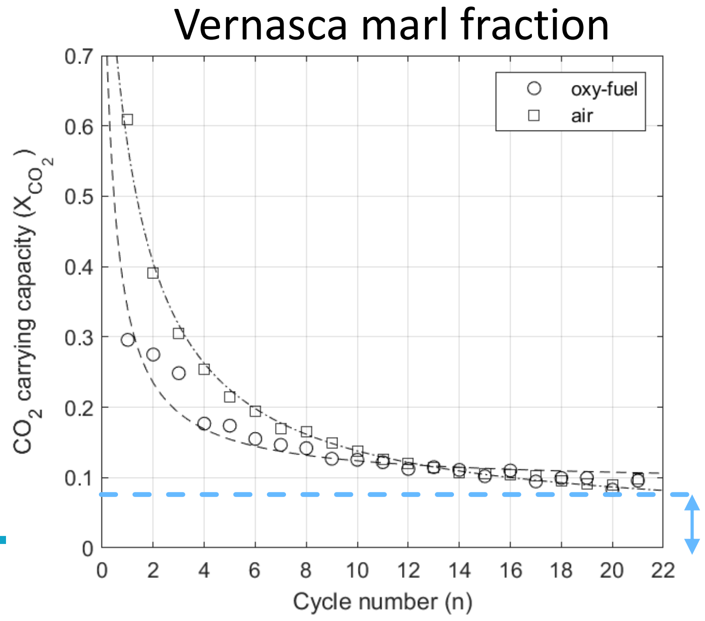


1. Sorbent studies at USTUTT: Cycle experiments

Results:

- additionally, the two main components of the Vernasca raw meal were investigated separately
- Marl fraction of the raw meal:
  - Residual activity not dependent from the reaction conditions
  - Much lower residual activity compared to limestone fraction
  - → Predominantly responsible for the deactivation of the Vernasca raw meal



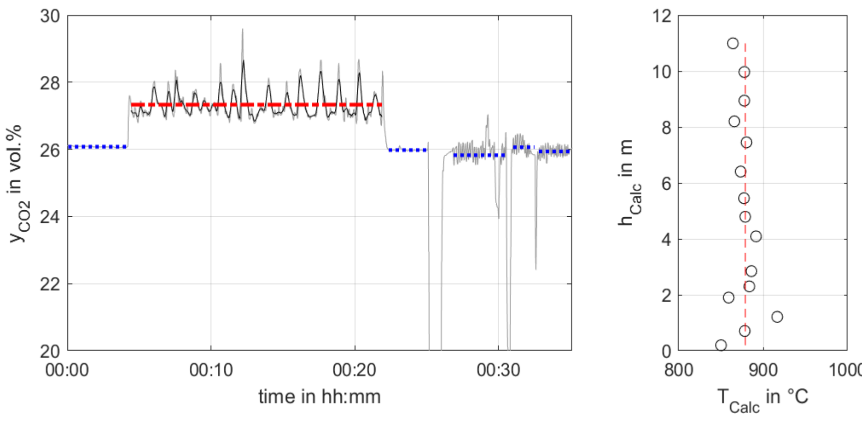


2. Sorbent studies at USTUTT: Calcination experiments in entrained flow reactor

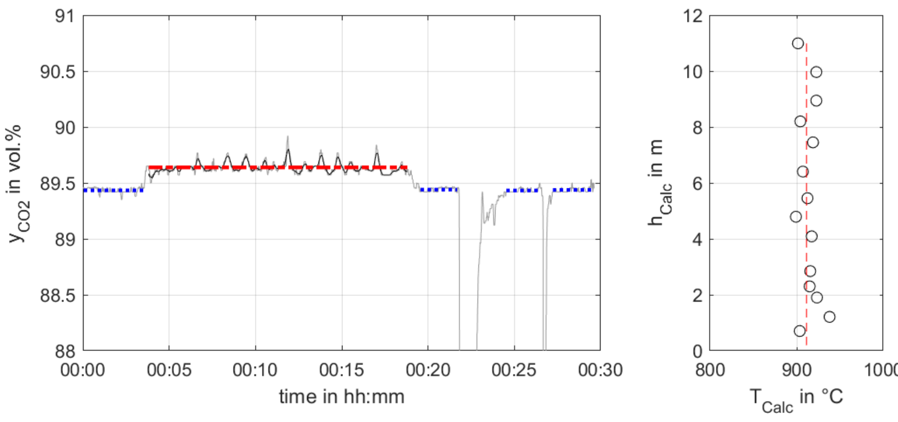
Properties of calcination experiments:

- Test rig:
  - Electrically heated, 120 kW_{el}
  - 12.4 m height, 68 mm diameter
- Three different setups:
  - Air calcination at 860°C and CO_2 concentration of 0.26 m³/m³
  - Oxy-fuel calcination at 900°C and CO_2 concentration of ~0:90 m³/m³
  - Oxy-fuel calcination at 920°C and CO_2 concentration of ~0:90 m³/m³

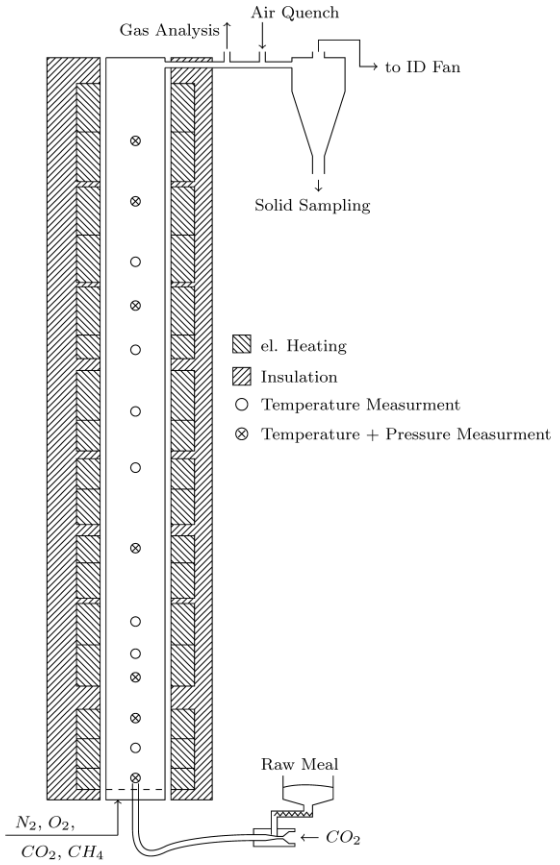
Air calcination



Oxy-fuel calcination



Experimental setup

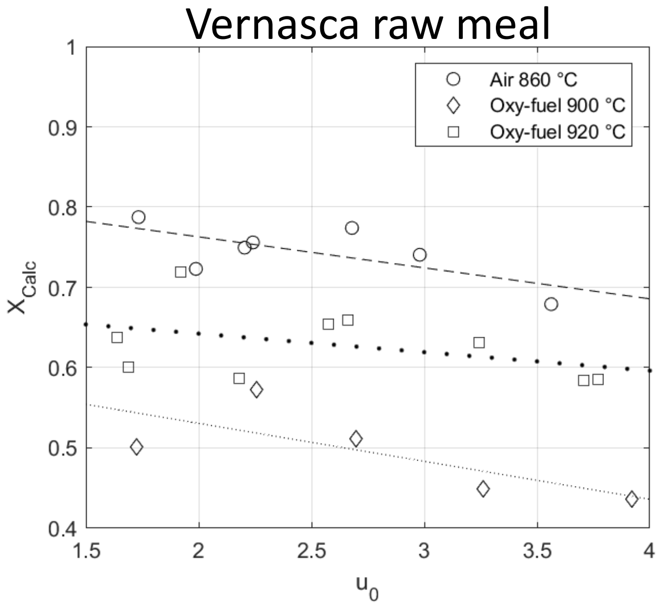


USTUTT's entrained flow reactor

Results:

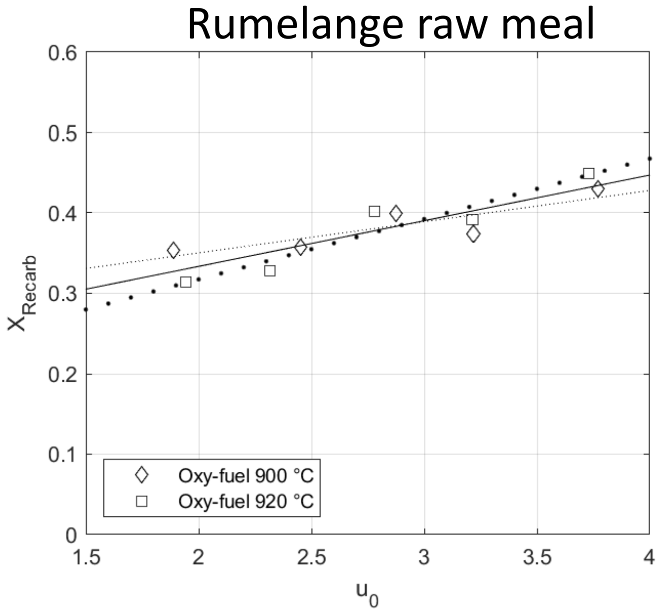
Calcination Degree

- Common trends over different raw meals:
  - Calcination kinetics improve with higher temperature
  - Calcination rate increases with reaction time



Recarbonation Degree

- Common trends over different raw meals:
  - Higher ability to absorb CO_2 with increasing velocity (i.e. shorter residence time)
  - Samples from oxy-fuel calcination: no significant influence of the calcination temperature on the recarbonation observable



Conclusions

- The **performance of raw meals** in all gas-solid reaction CaL-Systems **strongly depend on their chemical and physical composition** and level of aggregation of Ca/Si atoms

- **Carbonation:**
  - Active fraction of CaO, kinetics of carbonation, sulfation rates and belite formation rates can be determined by TG analysis
  - Carbonation rate is shown to be proportional to the CO_2 carrying capacity of the sorbent, regardless the origin of the calcined material under the experimental conditions tested
  - Marl fraction of the raw meal predominantly responsible for the deactivation of the Vernasca raw meal
- **Calcination:**
  - Calcination in oxy-fuel conditions requires drop tube / entrained flow apparatus
  - Within short gas-solid contact times, reasonable calcination rates possible
  - Dependency of calcination rate and surface area of the carbonate, activation energy and the standard enthalpy of $CaCO_3$ decomposition noticeable

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement n. 764816

This work is supported by the China Government (National Natural Science Foundation of China) under contract No.91434124 and No.51376105

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