CLEAN clinKER by calcium looping for low-CO_2 cement

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20-21 January 2020 – Geleen (The Netherlands)

8th High Temperature Solid Looping Cycles Network Meeting

Determination of intrinsic calcination kinetics of limestone-containing materials under rich atmospheres of CO_2

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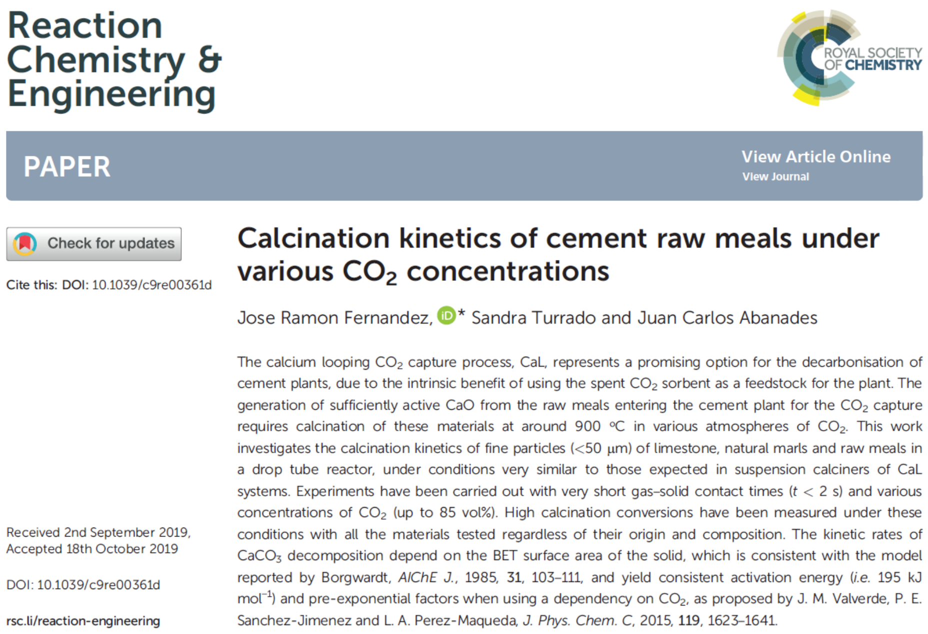
Summary

1. Experimental section: "drop tube" set up and materials

2. Results from kinetic studies of calcination in drop tube apparatus

3. Conclusions



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Cite this: DOI: 10.1039/c9re00361d

Calcination kinetics of cement raw meals under various CO_2 concentrations

Jose Ramon Fernandez,* Sandra Turrado and Juan Carlos Abanades

The calcium looping CO_2 capture process, CaL, represents a promising option for the decarbonisation of cement plants, due to the intrinsic benefit of using the spent CO_2 sorbent as a feedstock for the plant. The generation of sufficiently active CaO from the raw meals entering the cement plant for the CO_2 capture requires calcination of these materials at around 900 ºC in various atmospheres of CO_2. This work investigates the calcination kinetics of fine particles (<50 μm) of limestone, natural marls and raw meals in a drop tube reactor, under conditions very similar to those expected in suspension calciners of CaL systems. Experiments have been carried out with very short gas–solid contact times (t < 2 s) and various concentrations of CO_2 (up to 85 vol%). High calcination conversions have been measured under these conditions with all the materials tested regardless of their origin and composition. The kinetic rates of $CaCO_3$ decomposition depend on the BET surface area of the solid, which is consistent with the model reported by Borgwardt, *AIChE J.*, 1985, **31**, 103–111, and yield consistent activation energy (*i.e.* 195 kJ mol^{-1}) and pre-exponential factors when using a dependency on CO_2, as proposed by J. M. Valverde, P. E. Sanchez-Jimenez and L. A. Perez-Maqueda, *J. Phys. Chem. C*, 2015, **119**, 1623–1641.

Received 2nd September 2019,
Accepted 18th October 2019

DOI: 10.1039/c9re00361d

rsc.li/reaction-engineering

1. Experimental section. Drop tube set up

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Drop tube apparatus

- Reactor:

  L=6.5 m, ID=80 mm

  3 heating elements (3x3kW$_e$)
- Raw meal feeding:

  Air for solids transport (0.5 Nm^3/h, solids flow up to 8 kg/h)

  Preheated up to 500 ºC
- Inlet gas (Air/CO_2/steam) to reactor:

  Air (up to 90 Nm^3/h)

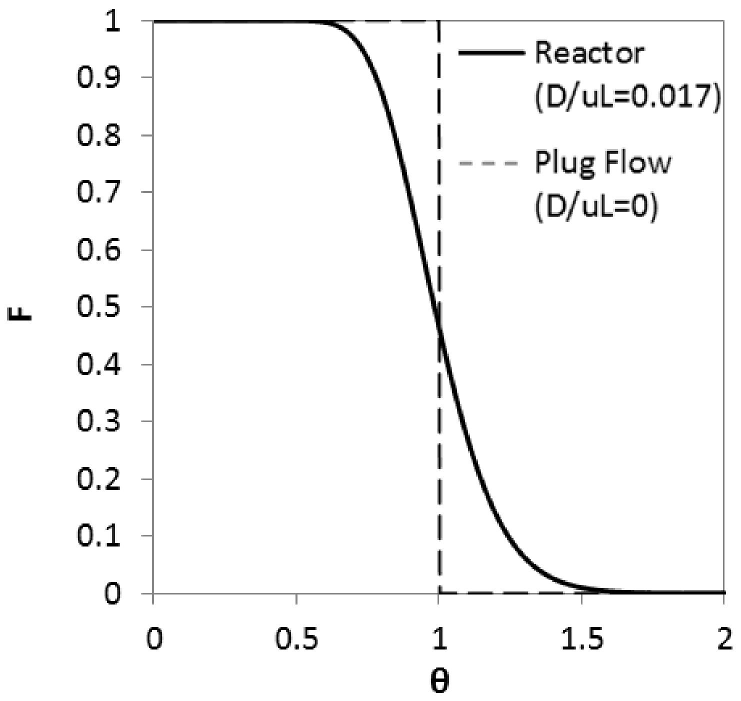
  Steam generator (up to 2.25 Nm^3 H_2O/h)

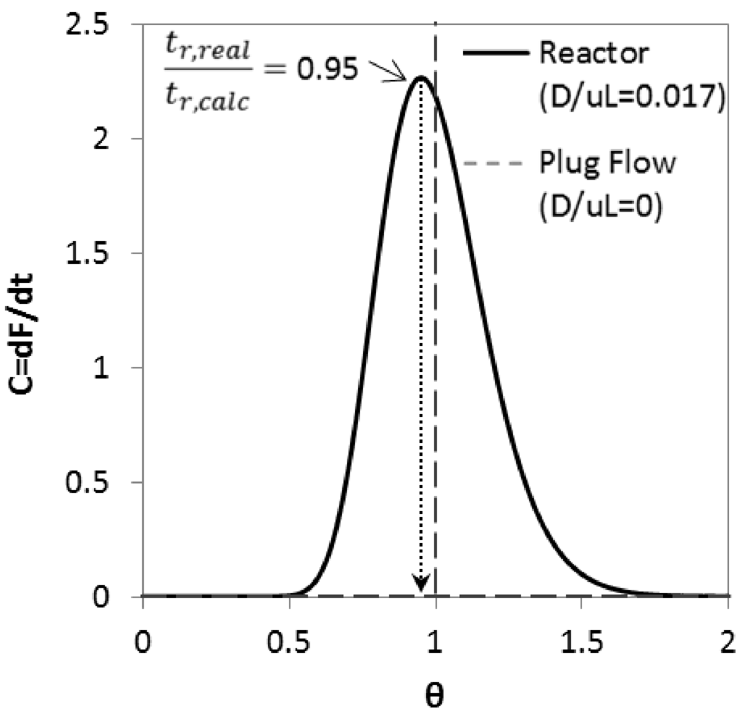
  Electric preheater of 3.5 kW$_e$ (T_{max} 1100ºC)
- Gas analysis:

  2 ABB analysers with IR modules+2 CO_2 meter sensors
- Solid analysis:

  LECO® CS230 (IR analysis)

Characterization of residence times in the drop tube furnace





RTD tests

- Step inputs using CO_2 as tracer
- Flow rate of 2.7 Nm^3/h (u_g=0.6 m/s) at 770 ºC
- Calculated dispersion number (D/uL) for the reactor of 0.017 (i.e. moderate dispersion)
- The resulting C curve (dF/t vs θ) shows that real residence time (t_r) ≈ t calculated as L/u_g

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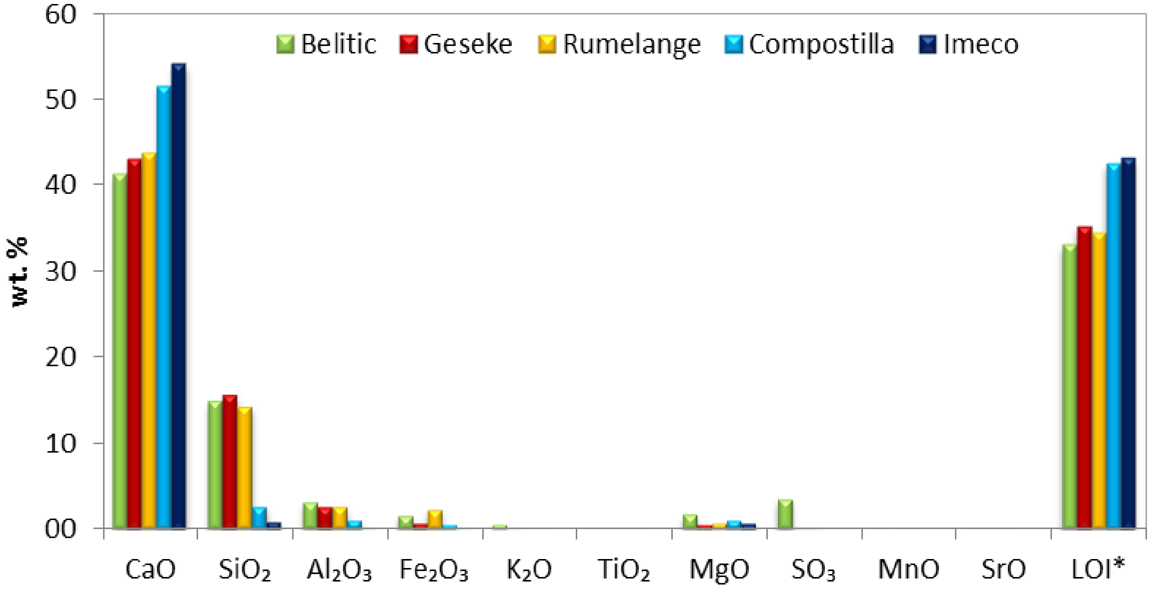
1. Physical and chemical characterization of fresh $CaCO_3$-based materials

13 Calcium-based raw meals materials tested

- **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

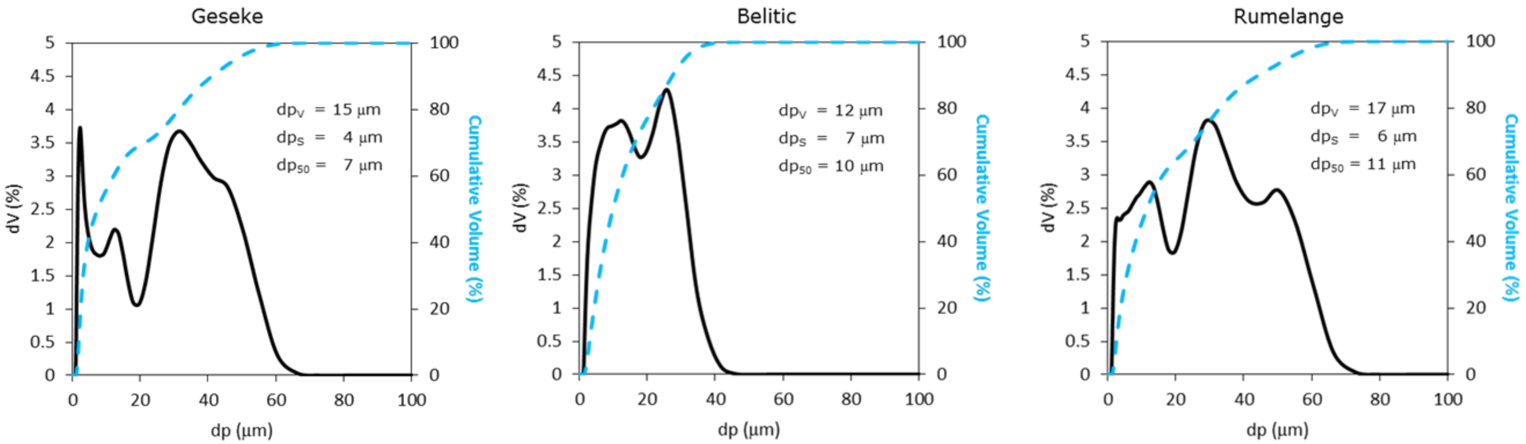
Chemical composition (XRF)



- 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)

1. Physical and chemical characterization of fresh $CaCO_3$-based materials

Particle size distribution



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

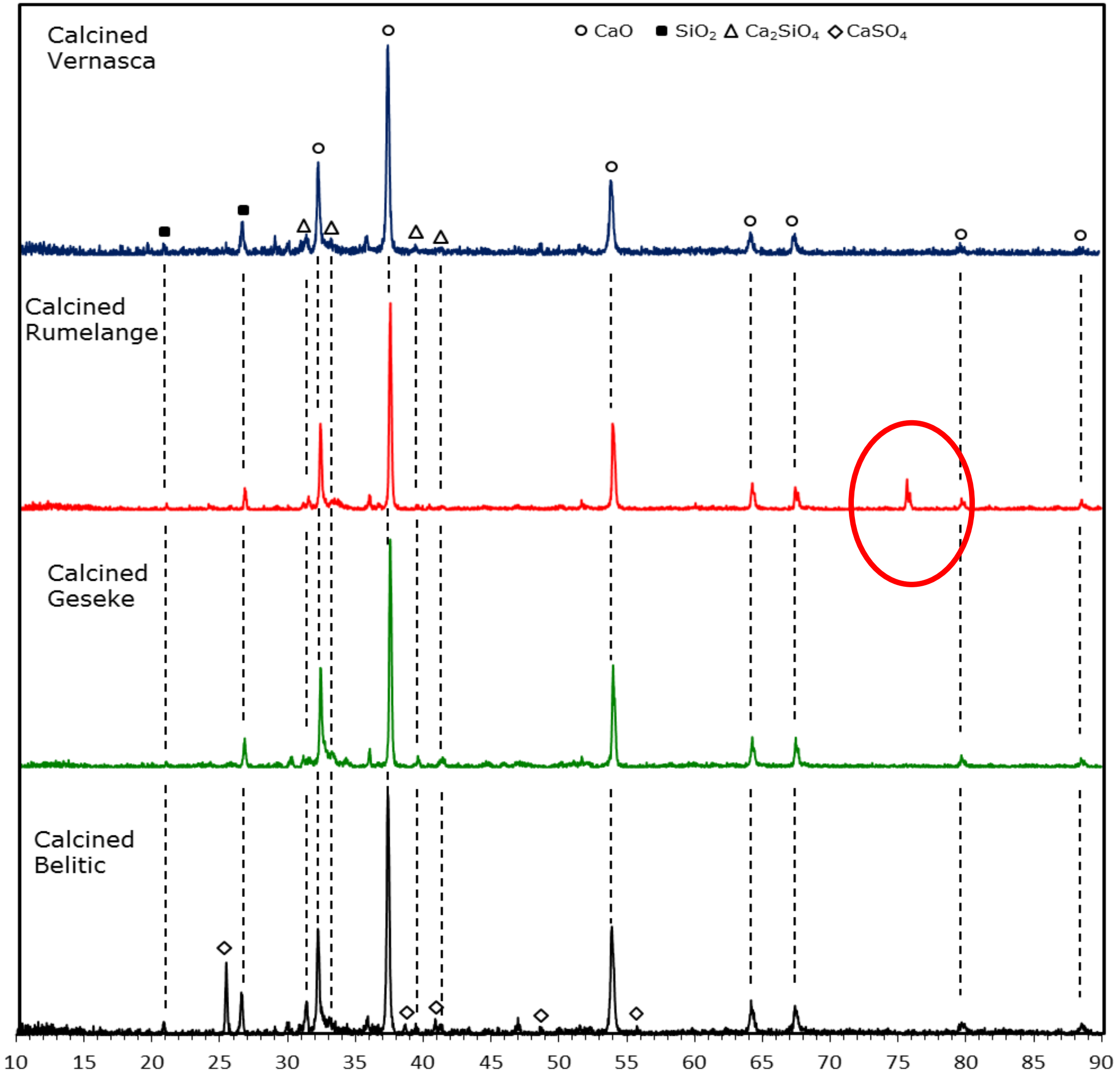
BET surface area

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).

1. Physical and chemical characterization of fresh $CaCO_3$-based materials

Crystalline phases (XRD)

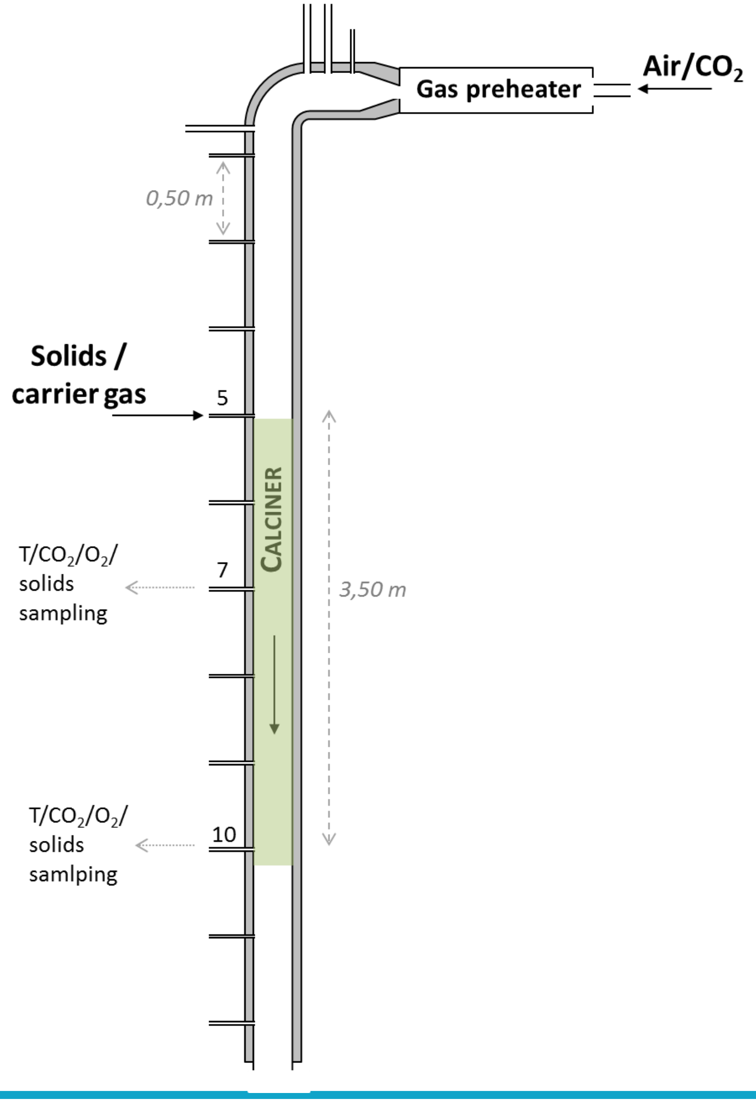


After calcination in air at 900º C for 10 min

- ✓ The main intensities correspond to CaO, SiO_2, $CaSO_4$
- ✓ The formation of belite is confirmed in all marl raw meals
- ✓ In Rumelange, there is a crystaline phase not identified yet

2. Experimental results: kinetic studies of calcination

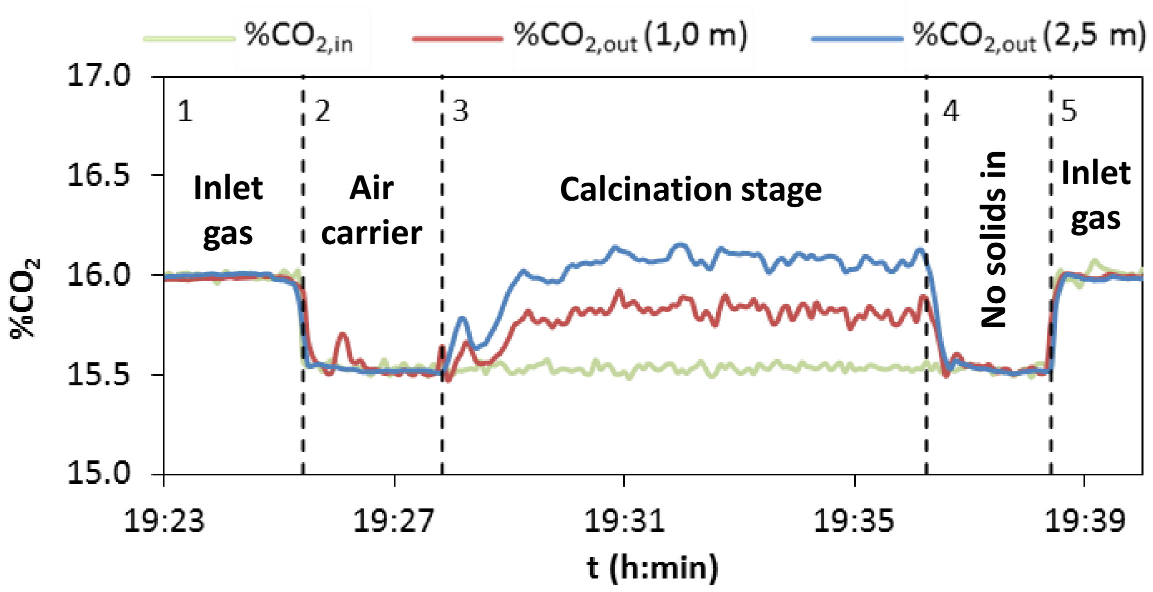
Experimental methodology



Main operating conditions tested in the drop tube

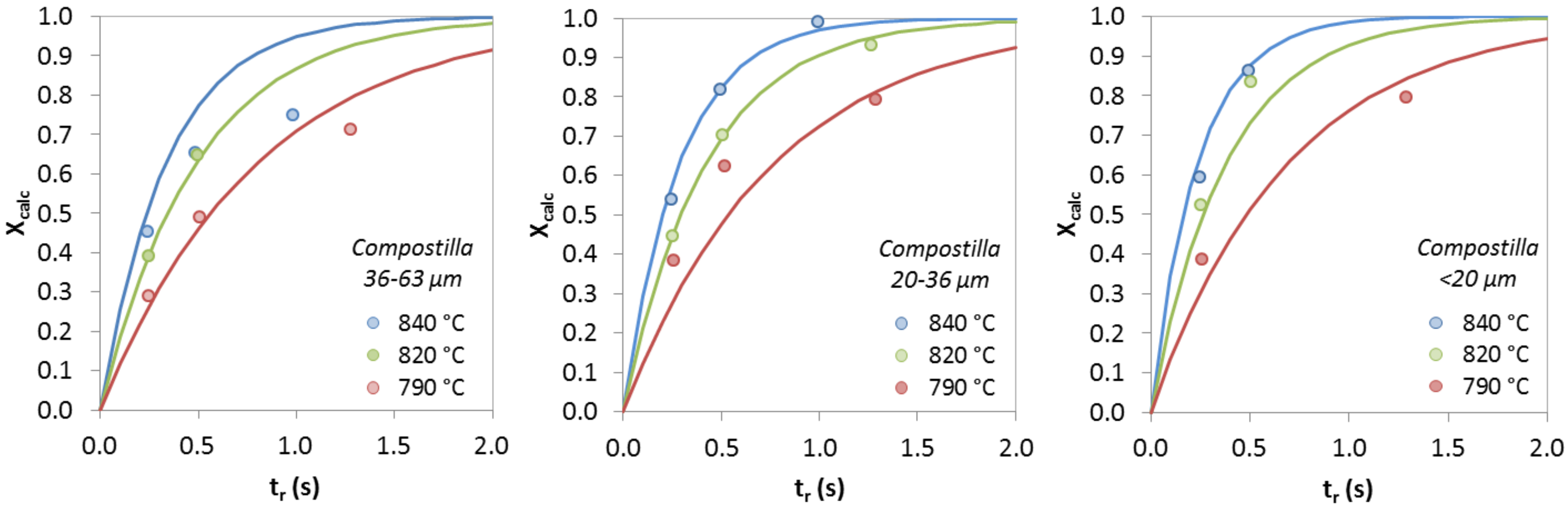
Calciner temperature (°C)	T_{calc}	790-1000
Calciner inlet velocity (m/s)	u_{calc}	1.1 - 2.2
Inlet CO_2 to the calciner	vol.%	0 - 90
Solids flowrate (kg/h)	$\dot{m}_s$	0.2 - 1.0

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

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)

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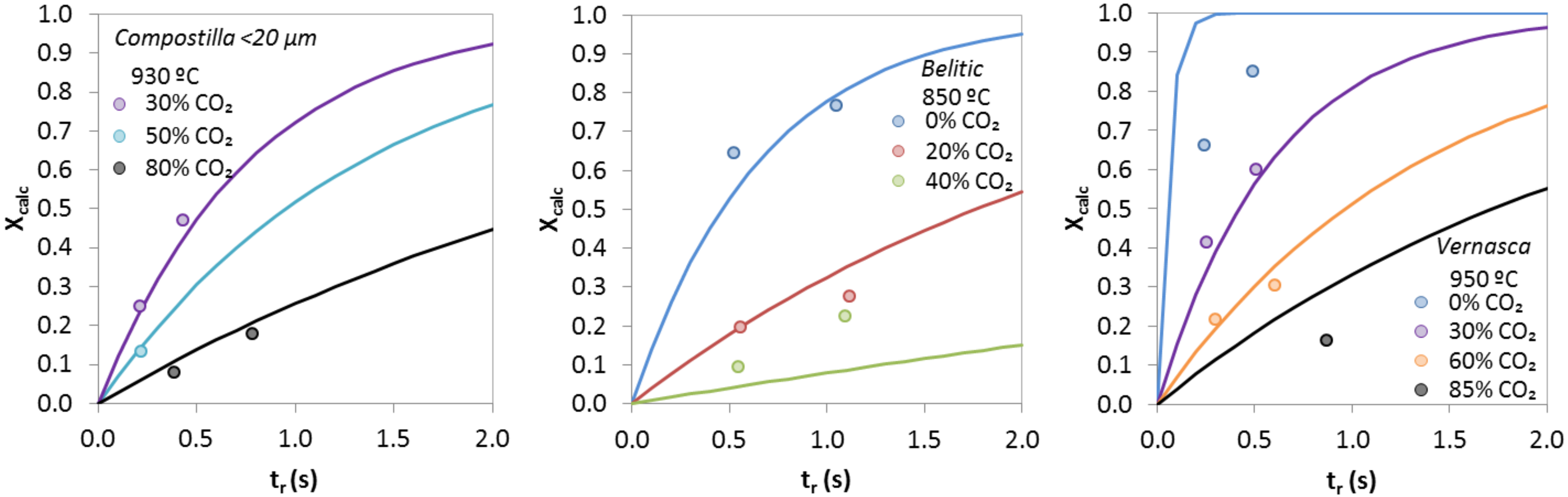
2. Experimental results: kinetic studies of calcination

Effect of **CO_2 content** on calcination kinetics



- Increasing contents of CO_2 in the gas phase hinder $CaCO_3$ calcination due to equilibrium restrictions
- However, relevant X_{calc} can be achieved under high CO_2 concentrations even at very short reaction times

Material	X_{calc}	tr (s)	T (ºC)	CO_2 v.%
Compostilla (<20µm)	0.2	0.8	930	80
Belitic	0.2	1.2	850	40
Vernasca	0.2	0.8	950	85

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2. Experimental results: kinetic studies of calcination

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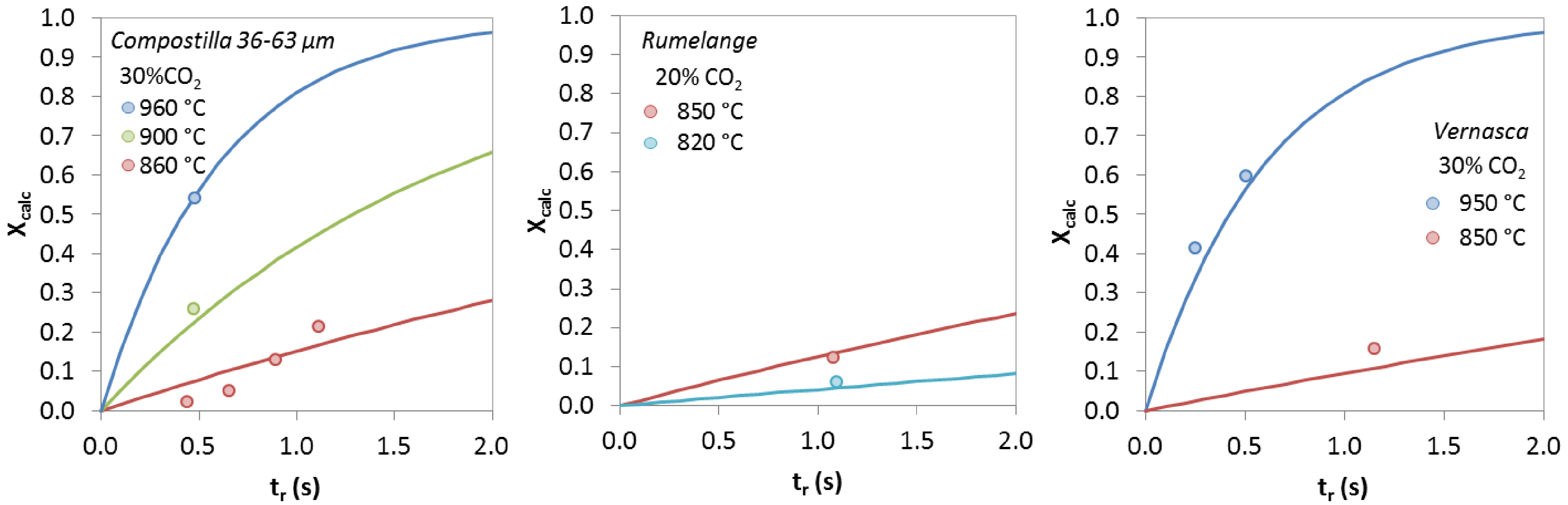
Effect of **temperature** on calcination kinetics



- Temperature dependencies affected by both Arrhenius and temperature effects on equilibrium of CO_2 CaO

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2. Kinetic studies of calcination

Kinetic model

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

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

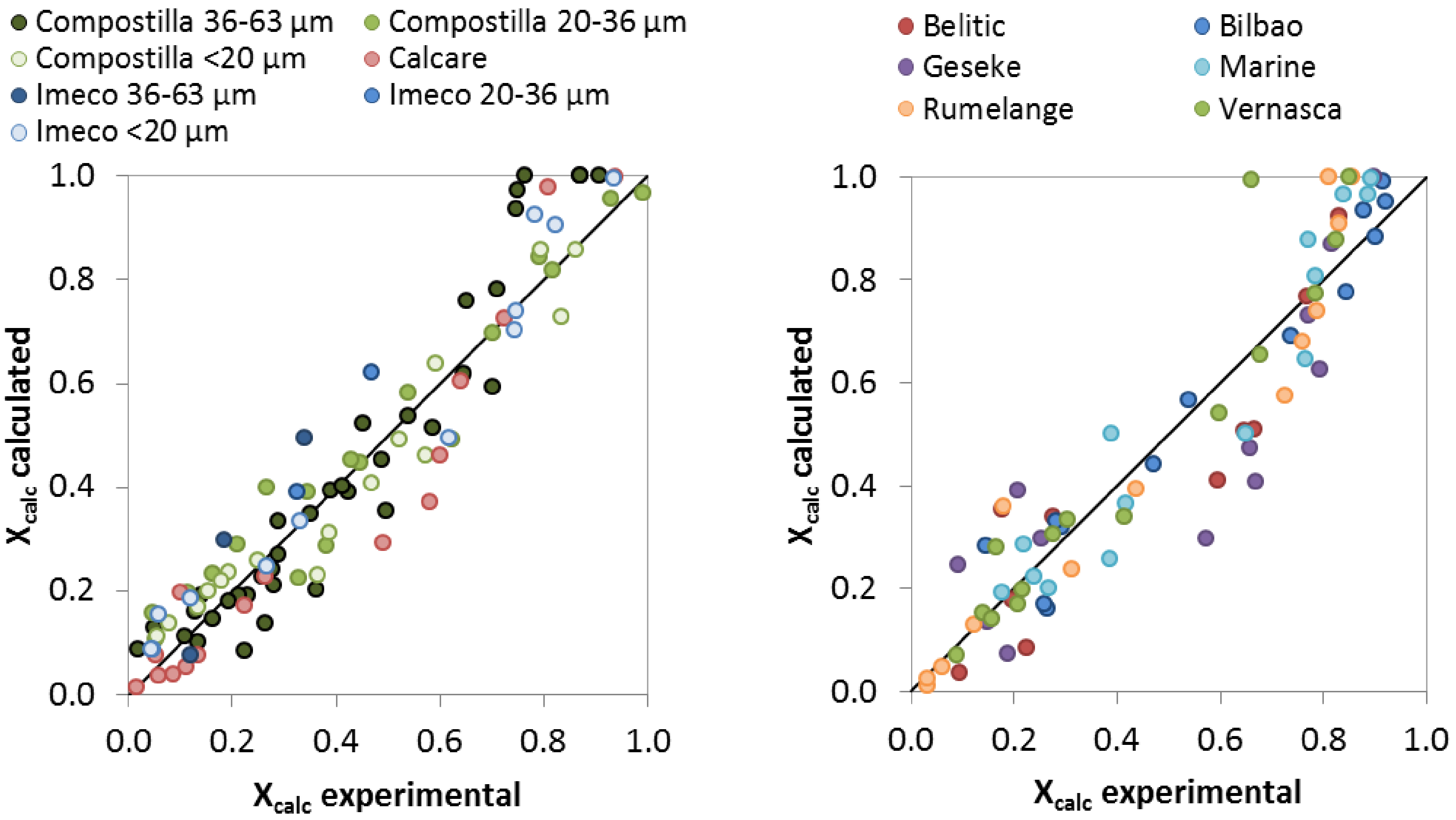
$$X_{calc} = 1 - e^{-a_1 e^{(-E_1/RT)} \left(1 - \frac{\nu_{CO2}}{\nu_{CO2,eq}}\right) \frac{1}{1 + A_1 e^{(-\Delta_1 H^0/RT)} \frac{\nu_{CO2}}{\nu_{CO2,eq}}} S_g t_r}$$

194.5 kJ/mol (Borgwardt, 1985) — 150 kJ/mol (Valverde et al., 2015)

Material	a_1 (mol/m²s)	A_1 (-)
Compostilla	$11.7 \cdot 10^6$	$153 \cdot 10^6$
Imeco	$45.8 \cdot 10^6$	$152 \cdot 10^6$
Calcare	$11.9 \cdot 10^6$	$219 \cdot 10^6$
Vernasca	$2.9 \cdot 10^6$	$137 \cdot 10^6$
Marine	$3.0 \cdot 10^6$	$43 \cdot 10^6$
Geseke	$5.8 \cdot 10^6$	$66 \cdot 10^6$
Rumelange	$4.9 \cdot 10^6$	$239 \cdot 10^6$
Belitic	$1.6 \cdot 10^6$	$28 \cdot 10^6$
Bilbao	$9.6 \cdot 10^6$	$27 \cdot 10^6$

2. Kinetic studies of calcination

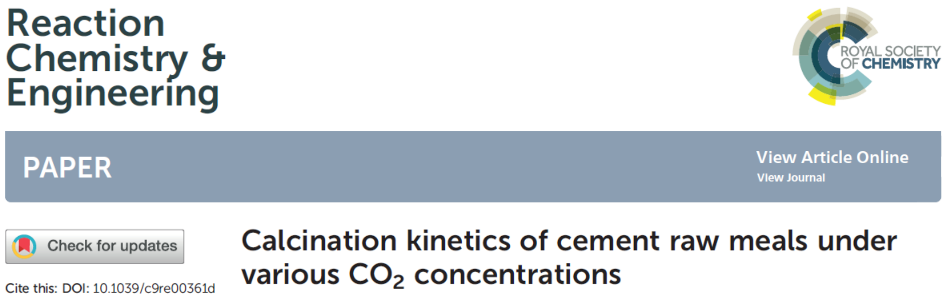
Experimental vs. model



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

3. Conclusions

- The drop tube apparatus used in this work can reproduce “classic” intrinsic kinetic parameters (i.e. obtained by Borgward et al. 1985) under air calcination conditions
- For raw meals and limestone calcined around T>900 ºC and t_r≈0.5 s, almost total calcination is achieved when operating with air. Relevant calcination conversions of 0.25 were measured under CO_2 concentrations up to 80 vol.% under the same conditions.
- The calcination rates of raw meals and limestones is well described by combining the models by Borgwardt (1985) and Valverde et al. (2015): reaction rates seem to depend on the BET surface area of the carbonate, activation energy and the standard enthalpy change of $CaCO_3$ decomposition are around 195 and 150 kJ/mol.
- Kinetics of calcination does not seem to represent a barrier for oxy-fired based, integrated calcium looping systems in cement plants.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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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